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LECTURE NOTES

FOR

CHEMICAL STUDENTS.

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TABLE OF CONTENTS.

CHAPTER I.

ORGANIC CHEMISTRY.

Page

Introductory 1
Compound organic radicals 2
Notation of organic compounds 3
Types of organic compounds 4
Reduction and development of formulæ 6
Classification of organic compounds 8

CHAPTER II.

ORGANIC RADICALS.

Class I. *Positive radicals* 9
Monad radicals of the methyl series 10
Normal, secondary, and tertiary monad radicals . . . 10
Ethyl 12
Monad radicals of the vinyl series 13
Monad radicals of the phenyl series 14

CHAPTER III.

ORGANIC RADICALS (*continued*).

Dyad positive radicals of the ethylene series 16
Isomerism of ethylene and ethylidene compounds . . . 19
Ethylene 20
Dyad positive radicals of the acetylene series . . . 21
Dyad positive radicals of the phenylene series . . . 24
Triad positive radicals 25

CHAPTER IV.

ORGANIC RADICALS (*continued*).

Class II. *Negative radicals* 25
Cyanogen 27
Hydrocyanic acid 27
Single and double cyanides 29
Other compounds of cyanogen 32

Page
Oxatyl 32
Relations between methyl, oxatyl, and cyanogen 33
Oxalic acid 34
Oxamic acid and oxamide 35

CHAPTER V.

HYDRIDES OF THE ORGANIC RADICALS.

Class I. *Hydrides of the positive radicals* 37
Hydrides of the radicals of the methyl series 37
Methylic hydride, or marsh-gas 39
Ethylic and amylic hydrides 40
Paraffin 41
Hydrides of the radicals of the phenyl series................ 42
Benzol 44
Substitution derivatives of benzol 45
Class II. *Hydrides of negative radicals* 49
Cyanic hydride or hydrocyanic acid 49
Oxatylic hydride or formic acid 49

CHAPTER VI.

THE ALCOHOLS.

Definition of alcohols.. 49
Classification of alcohols 50
Normal monohydric alcohols of the methyl series 52
Relations of these alcohols to the monad C_nH_{2n+1} radicals 53
„ „ „ „ dyad C_nH_{2n} radicals 54
„ „ „ „ hydrides of the C_nH_{2n+1} radicals 55
„ „ „ „ radical cyanogen. Ascent of the alcohol series 55
Methylic alcohol 56
Ethylic alcohol 57
Mercaptan 59
Propylic, butylic, and amylic alcohols 59
Secondary monohydric alcohols 60
Isopropylic, pseudamylic, and pseudohexylic alcohols 60
Tertiary monohydric alcohols 62
Pseudobutylic alcohol 62

CHAPTER VII.

THE ALCOHOLS (*continued*).

Monohydric alcohols 63
Vinyl series 63
Vinylic alcohol 64
Allylic alcohol 65

Page

CHAPTER VIII.

THE ALCOHOLS (*continued*).

Monohydric alcohols 66
  Phenyl series 66
Normal alcohols of this series 67
  Benzylic alcohol 67
Tertiary alcohols 68
  Phenylic alcohol or carbolic acid 68
  Cresylic alcohol or creosote 70

CHAPTER IX.

THE ALCOHOLS (*continued*).

Dihydric alcohols or glycols 70
  Ethylic glycol 71
  Derivatives of ethylic glycol 72
  Polyethylenic glycols 73

CHAPTER X.

THE ALCOHOLS (*continued*).

Dihydric alcohols. Orcin series 74
  Hydroquinone 75
  Orcin 76

CHAPTER XI.

THE ALCOHOLS (*continued*).

Trihydric alcohols. Glycerin series 77
  Glycerin 78
  Relation of glycerin to isopropylic alcohol 79
  " " allylic alcohol 79
  Relations of glycerin to propylic glycol 79
  " " glyceric and tartronic acids 80
  " " acrylic acid 80

CHAPTER XII.

THE ALCOHOLS (*continued*).

Trihydric alcohols. Pyrogallic series 81
  Pyrogallin 82
  Other polyhydric alcohols 83

Page

CHAPTER XIII.

THE ETHERS.

Classification of ethers 85

Ethers of the monohydric alcohols, methyl series 85

  Methylic and ethylic ethers 87

  Ethylic sulphide 89

  Ethers of the vinyl and phenyl series 89

Ethers of the dihydric alcohols 90

  Ethylenic oxide 90

Ethers of the trihydric alcohols 92

  Glycylic ether 93

CHAPTER XIV.

THE HALOID ETHERS.

Classification of haloid ethers 93

Haloid ethers of the monad positive radicals 93

Methylic chloride and chloroform 99

Ethylic chloride and iodide 101

Haloid ethers of the dyad positive radicals 102

Classification of these ethers 102

  Ethylenic bromide 103

  Ethylenic cyanide 104

Haloid ethers of the triad positive radicals 104

Classification of these ethers 104

CHAPTER XV.

THE ALDEHYDES.

Classification of aldehydes 105

Formation and reactions of aldehydes 105

Aldehydes derived from the $C_nH_{2n+1}Ho$ series of alcohols 108

Acetic aldehyde 108

Aldehydes derived from the $C_nH_{2n-1}Ho$ series of alcohols 110

Acrolein or acrylic aldehyde 110

Aldehydes derived from the $C_nH_{2n-7}Ho$ series of alcohols 111

Benzoic aldehyde or oil of bitter almonds 111

CHAPTER XVI.

THE ACIDS.

Classification of organic acids 113

Monobasic acids and their classification 113

Acetic or fatty series 114

Normal acids of this series 115

  Formation of normal fatty acids 117

Page
Relations of these acids to the C_nH_{2n+1} series of radicals.... . 119
" " " $C_nH_{2n+1}Ho$ series of alcohols .. 120
" " " each other. Ascent of the series .. 121
Formic acid 121
Acetic acid 123
Propionic and butyric acids 125
Valeric acid 126
Secondary fatty acids....................... 128
Dimethacetic or isobutyric acid 128
Tertiary fatty acids 129
Trimethacetic acid............................ 129

CHAPTER XVII.

THE ACIDS. *Acrylic or Oleic Series.*

Classification of these acids 130
Formation of normal acids 131
Formation of secondary and oleline acids 131
Relations of the acrylic to the acetic series of acids.......... 132
Acrylic acid 133
Oleic acid 134

CHAPTER XVIII.

THE ACIDS. *Lactic Series.*

Definition of an acid of this series 134
Classification of these acids 135
Normal acids 135
Etheric normal acids.......................... 136
Secondary acids............................... 137
Etheric secondary acids 138
Normal oleline acids.......................... 139
Etheric normal oleline acids.................. 140
Secondary and etheric secondary oleline acids 140
Relations of the lactic to the acetic series of acids 142
Relations of the lactic to the acrylic series of acids.......... 142
Lactic acid................................... 143
Isomerism in the lactic series 143

CHAPTER XIX.

THE ACIDS (*continued*).

Pyruvic Series 151
Relation of these acids to oxalic acid 152
Relation of these acids to the lactic series.................. 152
Glyoxylic series 152
Relation of these acids to the glycerin series of alcohols...... 153

Page

CHAPTER XX.

THE ACIDS. *Benzoic or Aromatic Series.*

Formation of these acids 153
Acryloid and lactoid acids of the benzoic series 155
Benzoic acid 157

CHAPTER XXI.

THE ACIDS. *Dibasic Acids.*

Constitution of these acids 158
Classification of dibasic acids 159
Succinic series 159
Relations of the succinic to the lactic series and to the glycols 161
Relations of the succinic series to the dyad radicals 161
Relations of the succinic to the acetic series 162
Succinic acid 163
Salts of succinic acid 165

CHAPTER XXII.

THE ACIDS. *Fumaric or Acryloid Series.*

Constitution of these acids 166
Isomerism in this series 167
Fumaric, maleic, and isomaleic acids 167
Itaconic, citraconic, and mesaconic acids 169

CHAPTER XXIII.

THE ACIDS. *Malic or Lactoid Series.*

Tartronic and malic acids 172
Tartaric or glyoxyloid series 173
Tartaric and homotartaric acids 173
Varieties of tartaric acid 173
Racemic, inactive tartaric, and metatartaric acids 174
Other series of dibasic acids 175
Alizaric acid or alizarin 177

CHAPTER XXIV.

THE ACIDS. *Tribasic Acids.*

Constitution and classification of the tribasic acids 177
Tricarballylic or acetoid series
Aconitic or acryloid series } 177
Citric or lactoid series
Tetrabasic and hexabasic acids 179
Pyromellitic and mellitic acids 179

Page

CHAPTER XXV.

THE ANHYDRIDES.

Constitution and classification of the anhydrides 181
Anhydrides of monohydric monobasic acids 182
Anhydrides of dihydric monobasic acids 183
Anhydrides of dihydric dibasic acids 184

CHAPTER XXVI.

THE KETONES.

Derivation and constitution of the ketones 184
Formation of the ketones 185
Isomerism in the ketone family 187

CHAPTER XXVII.

ETHEREAL SALTS.

Definition and constitution of the ethereal salts 188
Ethereal salts of monobasic, dibasic, and tribasic acids 189
Ethereal salts of monohydric, dihydric, and trihydric alcohols 189

CHAPTER XXVIII.

ORGANIC COMPOUNDS CONTAINING TRIAD AND PENTAD NITROGEN OR THEIR ANALOGUES.

Classification of these compounds 190
Positive section. The amines 191
The aniline colours 198
The natural alkaloids 201
The phosphines, arsines, stibines, and bismuthines 202
The oxybases 204

CHAPTER XXIX.

ORGANIC COMPOUNDS OF TRIAD NITROGEN (*continued*).

Neutral section. The amides 205
The alkalamides 209
The trichlorinated and tribrominated amines 209
The haloid compounds of oxybases 210
Negative section. The imides and nitrides 210

Page

CHAPTER XXX.

COMPOUNDS OF PENTAD NITROGEN AND ITS ANALOGUES.

Classification of these bodies 211
Positive compounds 211
Caustic nitrogen, phosphorus, arsenic, and antimony bases.... 211
Oxyarsenic and oxyantimonic bases 211
Neutral compounds........................ 212
Salts of amines, normal, monacid, and diacid 212
Salts of phosphines, arsines, and stibines 214
Salts of oxyarsenic and oxyantimonic bases 214
Negative compounds 214
Organic arsenic acids, oxychlorides, and chlorides 214
Organic antimonic acids 215

CHAPTER XXXI.

ORGANO-BORON AND SILICON COMPOUNDS.

Definition of organo-boron compounds 215
Boric methide and ammonia-boric methide 216
Boric ethide 217
Boric ethodiethylate and ammonia-boric ethide 218
Organo-silicon compounds 218
Silicic methide and silicic ethide........................ 221
Silicic triethohydrate and silicopropionic acid 222

CHAPTER XXXII.

ORGANOMETALLIC BODIES.

Definition of these compounds........................ 223
Formation of organometallic bodies 225
Reactions of organometallic bodies........................ 227
Constitution of organometallic bodies........................ 231
Organo-compounds containing monad and dyad metals 234
Organo-compounds containing triad, tetrad, and pentad metals. 235

ERRATUM.

Page 169, line 5 from bottom, *for* "eleven" *read* "fourteen."

LECTURE NOTES

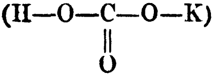
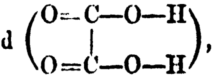
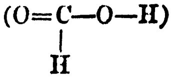
FOR

CHEMICAL STUDENTS.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

THE name *organic* is commonly restricted, by chemists, to compounds the molecules of which consist of one or more atoms of carbon *directly* combined either with carbon, nitrogen, or hydrogen. Thus, according to this definition, carbonic anhydride ($O{=}C{=}O$) and hydric potassic carbonate  $(H{-}O{-}\underset{\substack{\| \\ O}}{C}{-}O{-}K)$ are mineral or inorganic compounds, because the carbon which they contain is directly combined with oxygen only; but oxalic acid  $\left(\begin{array}{l}O{=}C{-}O{-}H\\ \quad\ \ |\\ O{=}C{-}O{-}H\end{array}\right)$, cyanic acid ($N{\equiv}C{-}O{-}H$), and formic acid  $(O{=}\underset{\substack{| \\ H}}{C}{-}O{-}H)$ are organic compounds, because their molecules contain carbon directly combined, in the first case with carbon, in the second with nitrogen, and in the third with hydrogen.

The number of elements usually entering into the composition of organic compounds is very small.

A large number of these compounds consist of carbon united with only *one* other element, either hydrogen or, rarely, nitrogen.

The members of another very large class contain only *three* elements:—carbon, hydrogen, and oxygen; carbon, hydrogen, and nitrogen; or carbon, nitrogen, and oxygen.

Others contain *four* elements—carbon, hydrogen, oxygen, and nitrogen.

Some contain sulphur, chlorine, bromine, iodine, silicon, phosphorus, boron, or metals ; but these are comparatively rare.

Although the number of the elements entering into the composition of organic compounds is much smaller than that usually taking part in the formation of minerals, yet the complexity of the former class of compounds is frequently much greater.

There is no instance of an organic molecule containing but two single atoms, and only one containing three (hydrocyanic acid, HCN).

On the other hand, the number of atoms in a single organic molecule is sometimes very great. Thus :—

The molecule of	Spermaceti	contains	98	atoms.
„ „	Stearin	„	173	„
„ „	Margarin	„	217	„
„ „	Albumen	„	226	„
„ „	Protagon	„	384	„

In nearly all organic compounds *carbon is a tetrad.* It forms, therefore, with 1 atom of hydrogen a triad compound radical, which exists in chloroform $(\mathbf{C}^{iv}H)'''Cl_3$; a dyad compound radical with 2 atoms of hydrogen, as in methylenic dichloride $(\mathbf{C}^{iv}H_2)''Cl_2$; and a monad compound radical with 3 atoms of hydrogen, as in methylic iodide $(\mathbf{C}^{iv}H_3)I$. But in these compounds it will be seen that the carbon is always saturated and always a tetrad.

This is in conformity with the following general law :—"In every molecule of a chemical compound the sum of the bonds is always an even number," because every number, whether odd or even, when multiplied by 2 gives an even number. To this may be added the following law, to which no exception is known :—"The sum of the bonds in any molecule is at least twice as great as the active atomicity of the most polyad element in the compound."

A compound organic radical is a group of atoms containing one *or more atoms of carbon of which one or more bonds are unsatisfied; and it is either a monad, dyad, &c. radical, according to the number of monad atoms required to complete its active atomicity.*

Such a radical, when a monad, triad, or pentad, cannot exist as a separate group; like hydrogen or nitrogen, when isolated, it combines with another group of atoms like itself, forming a duplex molecule. It is only by this union of two semi-molecules that the vacated bonds can be satisfied.

The following are two of the principal series of compound organic radicals:—

	Monads.		Dyads.
Methyl...	$\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ or $\left\{\begin{matrix}Me\\Me\end{matrix}\right.$	Methylene...	CH_2 or Me''*.
Ethyl ...	$\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$ or $\left\{\begin{matrix}Et\\Et\end{matrix}\right.$	Ethylene ...	C_2H_4 or Et''.
Propyl ...	$\left\{\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right.$ or $\left\{\begin{matrix}Pr\\Pr\end{matrix}\right.$	Propylene ...	C_3H_6 or Pr''.
Butyl ..	$\left\{\begin{matrix}C_4H_9\\C_4H_9\end{matrix}\right.$ or $\left\{\begin{matrix}Bu\\Bu\end{matrix}\right.$	Butylene ...	C_4H_8 or Bu''.
Amyl ...	$\left\{\begin{matrix}C_5H_{11}\\C_5H_{11}\end{matrix}\right.$ or $\left\{\begin{matrix}Ay\\Ay\end{matrix}\right.$	Amylene ...	C_5H_{10} or Ay''.

Organic radicals are the analogues of the monad, dyad, and triad elements of mineral chemistry.

Such being the constitution of the organic radicals, we will now proceed to investigate their functions in organic compounds, and to examine the general plan upon which these compounds are, on the atomic hypothesis, built up.

We shall be assisted in our investigation if we reduce the formulæ of these compounds to a few types or fundamental forms. In doing this it is necessary to avoid, as far as possible, all empirical grouping of atoms. Our formulæ ought to express, as exactly as possible, how the elements are combined with each other. Thus in a compound containing $C_xH_yO_z$, the formula ought to show, first, whether the hydrogen is combined with carbon or with oxygen; or if combined with both, it should indicate how many atoms are united with carbon, and how many with oxygen. Secondly, the formula ought to show whether the oxygen is united with carbon or with hydrogen, or partly with the one and partly with the other, or, lastly, whether it is performing the function of linking hydrogen to carbon.

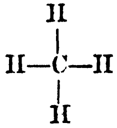
---

* Only known in combination.

This information is most completely given, in notation, by making carbon the dominant or grouping element in non-nitrogenous compounds, and nitrogen in the remaining organic compounds.

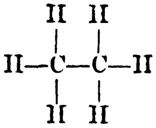
Non-nitrogenous organic compounds, exclusive of organo-metallic bodies and organo-boron and silicon compounds, can be conveniently considered under the two following types, viz. :—

1. The monadelphic, or marsh-gas type ....



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$$

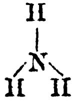
2. The diadelphic, or methyl type ...



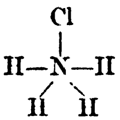
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Nitrogenous organic compounds arrange themselves in the most convenient manner under the two following types :—

3. The ammonia type ....

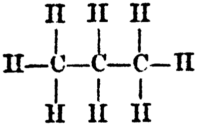


4. The ammonic-chloride type ......

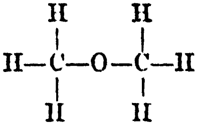


In addition to these types a few others will be occasionally necessary, such as :—

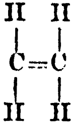
5. The triadelphic type ....



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

6. The double monadelphic type ... 

$$\begin{matrix} & H & & H & \\ & | & & | & \\ H- & C & -O- & C & -H \\ & | & & | & \\ & H & & H & \end{matrix}$$

7. The condensed diadelphic or olefine type.................... 

$$\begin{matrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{matrix}$$

Double, and sometimes even treble ammonia and ammonic-chloride types are required for certain compounds, but they do not need special description here.

The above types are written symbolically as follows:—

1. Monadelphic type.................... CH_4.
2. Diadelphic type .... $\left\{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right.$.
3. Ammonia type...................... $N'''H_3$.
4. Ammonic-chloride type .... $N^{v}H_4Cl$.
5. Triadelphic type .... $\left\{\begin{matrix} CH_3 \\ CH_2 \\ CH_3 \end{matrix}\right.$.
6. Double monadelphic type .. .. $\left\{\begin{matrix} CH_3 \\ O \\ CH_3 \end{matrix}\right.$.
7. Condensed diadelphic type ......″ $\left\{\begin{matrix} CH_2 \\ CH_2 \end{matrix}\right.$.

In order to facilitate the use of these symbolic types, it is advisable to become familiarized with the symbols of the following analogues of hydroxyl, in addition to those already given for inorganic compound radicals at p. 28 of vol. i., and for the monad and dyad radicals at p. 3 of the present volume:—

Methoxyl	CH_3O	or	Meo.
Ethoxyl	C_2H_5O	or	Eto.
Propoxyl..............	C_3H_7O	or	Pro.
Butoxyl	C_4H_9O	or	Buo.
Amoxyl	$C_5H_{11}O$	or	Ayo.

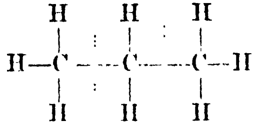
Formulæ written on the triadelphic type can be reduced to the diadelphic type, and those on the latter to the monadelphic type, as follows :—

$$\text{Propylic hydride.}\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}H_3\end{array}\right. = \mathbf{C}Me_2H_2 \text{ or } \mathbf{C}EtH_3.$$

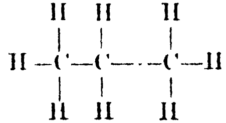
Triadelphic. Diadelphic. Monadelphic.

The above alternative monadelphic formulæ, although apparently different, are in reality identical, as can be easily proved by expressing both graphically, thus :—

$\mathbf{C}Me_2H_2$ =



$\mathbf{C}EtH_3$ =



On the other hand, monadelphic formulæ, if they contain a sufficient number of carbon atoms, can be expanded into diadelphic, triadelphic, &c. formulæ in the following manner :—

$$\mathbf{C}BuPrH_2 = \left\{\begin{array}{l}\mathbf{C}PrH_2\\ \mathbf{C}PrH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}EtH_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}EtH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}MeH_2\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2.\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{array}\right.$$

Normal butyl, or propylated methyl. (Molecule.)

This development of normal butyl depends on the following facts :—1st, that normal butyl is propylated methyl ; 2nd, that normal propyl is ethylated methyl ; and 3rd, that ethyl is methylated methyl.

Secondary and tertiary organic radicals (see p. 10) cannot be completely developed vertically :—

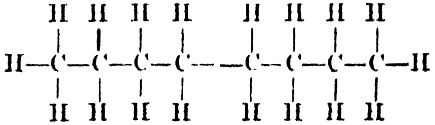
$$\left\{\begin{array}{l}\mathrm{CEtMeH}\\ \mathrm{CEtMeH}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{CMeH}\\ \mathrm{CMeH}\\ \mathrm{CMeH_2}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2}\\ \mathrm{CMeH}\\ \mathrm{CMeH}\\ \mathrm{CH_2}\\ \mathrm{CH_3}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2}\\ \mathrm{CH(CH_3)}\\ \mathrm{CH(CH_3)}\\ \mathrm{CH_2}\\ \mathrm{CH_3}\end{array}\right. :$$

Methylo-ethylated methyl. (Molecule.)

$$\left\{\begin{array}{l}\mathrm{CMe_3}\\ \mathrm{CMe_3}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CMe_2}\\ \mathrm{CMe_2}\\ \mathrm{CH_3}\end{array}\right. = \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{C(CH_3)(CH_3)}\\ \mathrm{C(CH_3)(CH_3)}\\ \mathrm{CH_3}\end{array}\right. \cdot$$

Trimethylated methyl. (Molecule.)

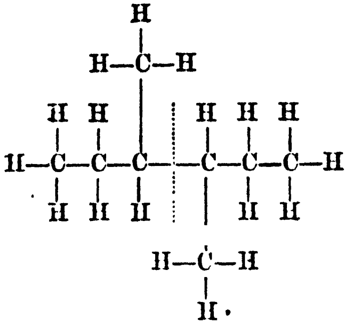
It will be seen, on comparing the above formulæ with the graphic representation of the respective compounds, that both express the same ideas of constitution. Thus in the developed symbolic formula of normal butyl it is evident that the two extreme carbon atoms are each united with three atoms of hydrogen and one of carbon, and all the intermediate carbon atoms with two of hydrogen and two of carbon, exactly as shown in the following graphic representation :—



$$\begin{array}{ccccccccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | & & | & & | & & & & | & & | & & | & & | \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — \mathrm{H} \\ & & | & & | & & | & & | & & & & | & & | & & | & & | \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \end{array}$$

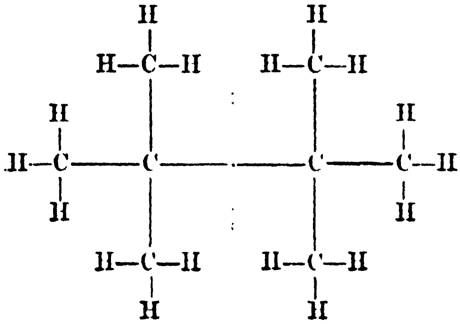
Normal butyl or propylated methyl. (Molecule.)

From the developed symbolic formula of methylo-ethylated methyl, it is evident that the two central carbon atoms are united with three atoms of carbon and one of hydrogen, that the two extreme carbon atoms are united with one atom of carbon and three of hydrogen, that the intermediate carbon atoms are joined to two hydrogen and two carbon atoms, and that the remaining carbon atoms are each combined with one atom of carbon, and three of hydrogen, thus:—



Methylo-ethylated methyl. (Molecule.)

Lastly, in the developed symbolic formula for trimethylated methyl, the two central atoms of carbon are each united with four carbon atoms, and all the remaining atoms of carbon are united with three of hydrogen and one of carbon, thus:—



Trimethylated methyl. (Molecule.)

CLASSIFICATION OF ORGANIC COMPOUNDS.

The most important organic compounds can be conveniently divided into the following thirteen families:—

1. Organic radicals.
2. Hydrides of organic radicals.

3. Alcohols.
4. Ethers.
5. Haloid ethers.
6. Aldehydes.
7. Acids.
8. Anhydrides.
9. Ketones.
10. Ethereal salts.
11. Organic compounds containing triad or pentad nitrogen.
12. Organo-boron and silicon compounds.
13. Organo-metallic bodies.

CHAPTER II.

ORGANIC RADICALS.

This family of organic compounds is divided into two classes:—

Class I. Positive radicals.
Class II. Negative radicals.

CLASS I.

POSITIVE RADICALS.

Monads.

Methyl or $(C_nH_{2n+1})_2$ Series.
Vinyl or $(C_nH_{2n-1})_2$ Series.
Phenyl or $(C_nH_{2n-7})_2$ Series.

Dyads.

Ethylene or C_nH_{2n} Series.
Acetylene or C_nH_{2n-2} Series.
Phenylene or C_nH_{2n-6} Series.

Triads.

Glyceryl or $(C_nH_{2n-1})'''_2$ Series.

CLASS I.

POSITIVE RADICALS.

MONADS.

METHYL or $(C_nH_{2n+1})_2$ *SERIES.*

These radicals are divided into three sections, viz. Normal, Secondary, and Tertiary:—

General formulæ.

1. Normal Radicals .... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_nH_{2n+1})H_2\end{array}\right.$.

2. Secondary Radicals ... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2H\\ \mathbf{C}(C_nH_{2n+1})_2H\end{array}\right.$.

3. Tertiary Radicals ...... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_3\\ \mathbf{C}(C_nH_{2n+1})_3\end{array}\right.$.

In the first of the above formulæ n may $=0$, but in the others it must be a positive integer.

Examples of the tertiary series of radicals may be seen in the tertiary fatty acids. They have not yet been isolated.

It is evident that, besides the three series of radicals shown above, three other series, containing, in the same molecule, normal and secondary, normal and tertiary, and secondary and tertiary radicals, may exist; but up to the present time only one or two examples of such radicals are known.

By the action of zincic ethide on the chloride obtained from acetone by means of phosphoric chloride, a hydrocarbon is obtained, which may be regarded as a mixed normal and tertiary monad positive radical: ethyl etho-dimethomethyl or ethyl isoamyl:—

$$\underbrace{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}MeCl_2\end{array}\right.}_{\text{Chloride from acetone.}} + \underbrace{ZnEt_2}_{\text{Zincic ethide.}} = \underbrace{ZnCl_2}_{\text{Zincic chloride.}} + \underbrace{\left\{\begin{array}{l}\mathbf{C}Me_2Et\\ \mathbf{C}MeH_2\end{array}\right.}_{\text{Ethyl ethodimethomethyl.}}$$

1. *Normal Radicals.*

This series contains the radicals of the methylic series of alcohols.

These radicals also enter into the composition of the normal series of fatty acids.

The following list contains all the radicals of this section that have been hitherto obtained:—

				Boiling-points.
Methyl	$\left\{\begin{matrix}\text{Me}\\ \text{Me}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_3\end{matrix}\right.$	....	not known.
Ethyl	$\left\{\begin{matrix}\text{Et}\\ \text{Et}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}\text{Me}H_2\\ \mathbf{C}\text{Me}H_2\end{matrix}\right.$,	or $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{matrix}\right.$	......about −23°.
Propyl	$\left\{\begin{matrix}\text{Pr}\\ \text{Pr}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}\text{Et}H_2\\ \mathbf{C}\text{Et}H_2\end{matrix}\right.$,	or $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}H_3\end{matrix}\right.$	.... +68°.
Butyl	$\left\{\begin{matrix}\text{Bu}\\ \text{Bu}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}\text{Pr}H_2\\ \mathbf{C}\text{Pr}H_2\end{matrix}\right.$	....	119°.
Amyl	$\left\{\begin{matrix}\text{Ay}\\ \text{Ay}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}\text{Bu}H_2\\ \mathbf{C}\text{Bu}H_2\end{matrix}\right.$	....	159°.
Caproyl	$\left\{\begin{matrix}\text{Cp}\\ \text{Cp}'\end{matrix}\right.$	or $\left\{\begin{matrix}\mathbf{C}\text{Ay}H_2\\ \mathbf{C}\text{Ay}H_2\end{matrix}\right.$	....	202°.

Preparation.—1. By the action of zinc on the iodides of the normal radicals:—

$$2\mathbf{C}(C_nH_{2n+1})H_2I \quad + \quad \text{Zn} \quad = \quad \mathbf{Zn}I_2 \quad + \quad \left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_nH_{2n+1})H_2\end{matrix}\right..$$

Part of the liberated radical is at the same time decomposed into the hydride of the radical and the corresponding dyad radical:—

$$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_nH_{2n+1})H_2\end{matrix}\right. \quad = \quad \left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ H\end{matrix}\right. \quad + \quad [\mathbf{C}(C_nH_{2n+1})H]''.$$

A remarkable special method for preparing ethyl consists in exposing mercury and ethylic iodide to the influence of sunlight:—

$$\underset{\text{Ethylic iodide.}}{2\text{EtI}} \quad + \quad \text{Hg} \quad = \quad \underset{\text{Mercuric iodide.}}{\mathbf{Hg}I_2} \quad + \quad \underset{\text{Ethyl.}}{\text{Et}_2}.$$

2. By the electrolysis of the salts of the normal fatty acids. In this process, nascent oxygen acts upon the fatty acid, converting its oxatyl into carbonic anhydride, the positive radical being set free:—

$$2\underset{\text{Fatty acid.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}OHo\end{matrix}\right.} + O = \underset{\text{Radical.}}{\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_nH_{2n+1})H_2\end{matrix}\right.}$$

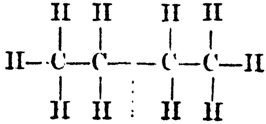
$$+ \underset{\text{Carbonic anhydride.}}{2\mathbf{C}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

3. By acting with zinc upon the iodides of two radicals simultaneously, the so-called double or mixed radicals are produced:—

$$\underset{\text{Methylic iodide.}}{MeI} + \underset{\text{Ethylic iodide.}}{EtI} + Zn = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Methyl ethyl.}}{\left\{\begin{matrix}Me\\ Et\end{matrix}\right.}.$$

ETHYL.

$$\left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}MeH_2\end{matrix}\right.$$



$$\begin{array}{c}H\ \ H\quad\ H\ \ H\\ |\ \ \ |\quad\ \ |\ \ \ |\\ H-C-C\ \vdots\ C-C-H\\ |\ \ \ |\quad\ \ |\ \ \ |\\ H\ \ H\quad\ H\ \ H\end{array}$$

Molecular weight =58. *Molecular volume* □□. 1 *litre of ethyl gas weighs* 29 *criths. Boils at about* −23° C.

Preparation.—By digesting together in a close vessel at 120° ethylic iodide and zinc, the reaction being similar to that between hydriodic acid and zinc:—

$$Zn + \underset{\text{Hydriodic acid.}}{2HI} = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Hydrogen.}}{\left\{\begin{matrix}H\\ H\end{matrix}\right.}.$$

$$Zn + \underset{\text{Ethylic iodide.}}{2EtI} = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Ethyl.}}{\left\{\begin{matrix}Et\\ Et\end{matrix}\right.}.$$

2. *Secondary Radicals.*

Two secondary monad positive radicals are known :—

Isopropyl............ $\left\{\begin{array}{l}\mathbf{C}Me_2H\\ \mathbf{C}Me_2H\end{array}\right.$ ....boils at 58°

Amyl-isopropyl ... $\left\{\begin{array}{l}\mathbf{C}Me_2H\\ \mathbf{C}BuH_2\end{array}\right.$ .... „ „ 110°

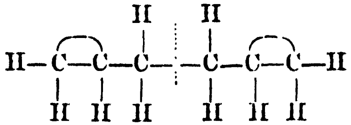
VINYL SERIES.

General formula... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n-1})H_2\\ \mathbf{C}(C_nH_{2n-1})H_2\end{array}\right.$.

The first member of this series, vinyl, has not yet been isolated.

ALLYL.

$$\left\{\begin{array}{l}\mathbf{C}_3H_5\\ \mathbf{C}_3H_5\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{C}(CMe''H)H_2\\ \mathbf{C}(CMe''H)H_2\end{array}\right..$$



Molecular weight =82. *Molecular volume* ☐☐. 1 *litre of allyl vapour weighs* 41 *criths. Sp. gr.* 0·684. *Boils at* 59°.

Preparation.—By digesting allylic iodide with sodium, and then distilling :—

$$Na_2 + 2\mathbf{C}(CMe''H)H_2I = \left\{\begin{array}{l}\mathbf{C}(CMe''H)H_2\\ \mathbf{C}(CMe''H)H_2\end{array}\right. + 2NaI.$$

Allylic iodide. Allyl. Sodic iodide.

Character.—Bromine and iodine unite directly with allyl, producing allylic tetrabromide and tetriodide. In these compounds the molecule of allyl plays the part of a tetrad radical.

In allylic tetrabromide, four latent carbon bonds in the molecule of allyl have become active, and have united with four atoms of bromine :—

$$\left\{\begin{array}{l}\mathbf{C}(CMe''H)H_2\\ \mathbf{C}(CMe''H)H_2\end{array}\right. + Br_4 = \left\{\begin{array}{l}\mathbf{C}[C(CH_2Br)BrH]H_2\\ \mathbf{C}[C(CH_2Br)BrH]H_2\end{array}\right..$$

Allyl. Allylic tetrabromide.

An analogous case is met with in ferric chloride, where two tetrad atoms, united by one bond of each, become together hexadic:—

$$\left\{\begin{array}{l}\mathbf{Fe}\mathrm{Cl}_3\\ \mathbf{Fe}\mathrm{Cl}_3\end{array}\right..$$

Allylic monobromide can only be obtained by the action of phosphorous tribromide on allylic alcohol:—

$$\underset{\text{Allylic alcohol.}}{3\mathbf{C}(\mathrm{CMe}''\mathrm{H})\mathrm{H}_2\mathrm{Ho}} + \underset{\substack{\text{Phosphorous}\\ \text{tribromide.}}}{\mathbf{P}\mathrm{Br}_3} = \underset{\text{Allylic monobromide.}}{3\mathbf{C}(\mathrm{CMe}''\mathrm{H})\mathrm{H}_2\mathrm{Br}}$$

$$+ \underset{\text{Phosphorous acid.}}{\mathbf{P}\mathrm{OHHo}_2}.$$

PHENYL SERIES.

General formula ... $\left\{\begin{array}{l}\mathbf{C}_n\mathrm{H}_{2n-7}\\ \mathbf{C}_n\mathrm{H}_{2n-7}\end{array}\right..$

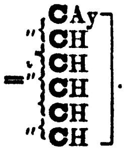
These radicals are but imperfectly known. The following have been isolated:—

Phenyl .... $\left\{\begin{array}{l}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}_6\mathrm{H}_5\end{array}\right..$

Tolyl............................ $\left\{\begin{array}{l}\mathbf{C}_6\mathrm{H}_4\mathrm{Me}\\ \mathbf{C}_6\mathrm{H}_4\mathrm{Me}\end{array}\right..$

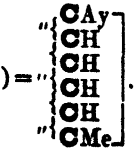
Benzyl .... $\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_2(\mathrm{C}_6\mathrm{H}_5)\\ \mathbf{C}\mathrm{H}_2(\mathrm{C}_6\mathrm{H}_5)\end{array}\right..$

Amyl benzol or amyl phenyl .. $\mathbf{C}_6\mathrm{H}_5(\mathrm{C}_5\mathrm{H}_{11})$ =

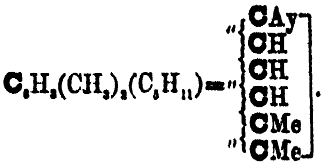


$$=\left[\begin{array}{l}\mathbf{C}\mathrm{Ay}\\ {}''\mathbf{CH}\\ \mathbf{CH}\\ {}''\mathbf{CH}\\ \mathbf{CH}\\ {}''\mathbf{CH}\end{array}\right].$$

Amyl toluol or amyl benzyl... $\mathbf{C}_6\mathrm{H}_4(\mathrm{CH}_3)(\mathrm{C}_5\mathrm{H}_{11})$ =



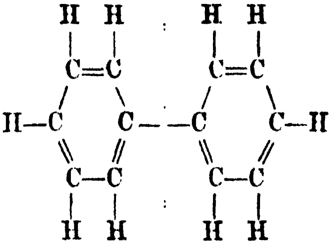
$$=\left[\begin{array}{l}{}''\mathbf{C}\mathrm{Ay}\\ {}''\mathbf{CH}\\ \mathbf{CH}\\ {}''\mathbf{CH}\\ \mathbf{CH}\\ {}''\mathbf{C}\mathrm{Me}\end{array}\right].$$

Amyl xylol. .... 

$$C_6H_3(CH_3)_2(C_5H_{11}) = \begin{matrix}'' \\ \\ \\ \\ \\ ''\end{matrix}\left\{\begin{matrix}CAy \\ CH \\ CH \\ CH \\ CMe \\ CMe\end{matrix}\right]$$.

PHENYL.

$$\left\{\begin{matrix}C_6H_5 \\ C_6H_5\end{matrix}\right.$$



Molecular weight =154. *Molecular volume* ☐☐. 1 *litre of phenyl vapour weighs* 77 *criths. Fuses at* 70°. *Boils at* 240°.

Preparation.—By the action of sodium on phenylic bromide:—

$$\underset{\text{Phenylic bromide.}}{2C_6H_5Br} + Na_2 = \underset{\text{Phenyl.}}{\left\{\begin{matrix}C_6H_5 \\ C_6H_5\end{matrix}\right.} + \underset{\text{Sodic bromide.}}{2NaBr.}$$

Reaction.—By treatment with bromine, phenyl produces bromphenyl and hydrobromic acid:—

$$\underset{\text{Phenyl.}}{\left\{\begin{matrix}C_6H_5 \\ C_6H_5\end{matrix}\right.} + Br_4 = \underset{\text{Bromphenyl.}}{\left\{\begin{matrix}C_6H_4Br \\ C_6H_4Br\end{matrix}\right.} + \underset{\text{Hydrobromic acid.}}{2HBr.}$$

CHAPTER III.

POSITIVE RADICALS.

DYADS.

ETHYLENE or $C_n H_{2n}$ *SERIES.*

Preparation.—These compounds are produced as follows:—

1. In many cases of destructive distillation, where, however, the reaction cannot be traced.

2. By the abstraction of the elements of water from the normal monohydric alcohols of the methylic series, as for instance:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} = {}'' \underset{\text{Ethylene.}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

3. By passing the vapours of the haloid compounds of the normal monad radicals of the C_nH_{2n+1} series over heated lime, thus:—

$$\underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.} = {}'' \underset{\text{Ethylene.}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

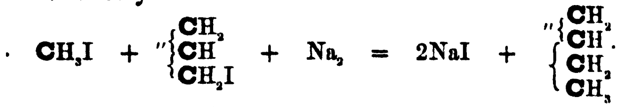
4. By the transformation of the monad radicals at the moment of liberation from their compounds, when they split into dyad radicals and the hydrides of monad radicals:—

$$\underset{\text{Ethyl.}}{\left\{\begin{matrix}C(CH_3)H_2\\C(CH_3)H_2\end{matrix}\right.} = {}'' \underset{\text{Ethylene.}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Ethylic hydride.}}{\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.}.$$

5. By the action of the iodide of a monad radical on the sodium compound of a monad radical:—

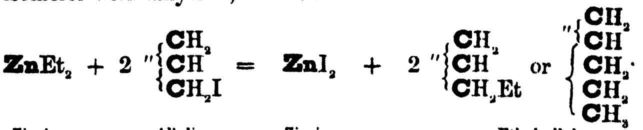
$$\underset{\text{Ethylic iodide.}}{\left\{\begin{matrix}CH_3\\CH_2I\end{matrix}\right.} + \underset{\text{Sodic ethide.}}{\left\{\begin{matrix}CH_3\\CH_2Na\end{matrix}\right.} = \underset{\text{Sodic iodide.}}{NaI} + {}'' \underset{\text{Ethylene.}}{\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Ethylic hydride.}}{\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.}.$$

6. Methylic iodide and allylic iodide dissolved in ether and digested with sodium in sealed vessels produce methyl-allyl, an isomer of butylene :—



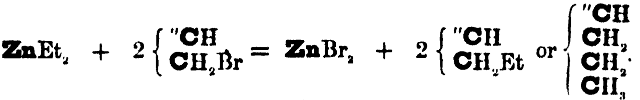
$$\underset{\text{Methylic iodide.}}{CH_3I} + \underset{\text{Allylic iodide.}}{{}''\left\{\begin{array}{l}CH_2\\CH\\CH_2I\end{array}\right.} + Na_2 = 2NaI + \underset{\text{Methyl-allyl.}}{{}''\left\{\begin{array}{l}CH_2\\CH\\CH_2\\CH_3\end{array}\right.}$$

7. By the action of zincic ethide on allylic iodide, ethyl-allyl, isomeric with amylene, is obtained :—



$$\underset{\text{Zincic ethide.}}{ZnEt_2} + 2\,\underset{\text{Allylic iodide.}}{{}''\left\{\begin{array}{l}CH_2\\CH\\CH_2I\end{array}\right.} = \underset{\text{Zincic iodide.}}{ZnI_2} + 2\,{}''\left\{\begin{array}{l}CH_2\\CH\\CH_2Et\end{array}\right. \text{ or } \underset{\text{Ethyl-allyl.}}{{}''\left\{\begin{array}{l}CH_2\\CH\\CH_2\\CH_2\\CH_3\end{array}\right.}$$

8. By treatment of vinylic bromide (brominated ethylene) with zincic ethide, ethyl-vinyl, isomeric with butylene, is produced :—



$$\underset{\text{Zincic ethide.}}{ZnEt_2} + 2\underset{\text{Vinylic bromide.}}{\left\{\begin{array}{l}''CH\\CH_2Br\end{array}\right.} = \underset{\text{Zincic bromide.}}{ZnBr_2} + 2\left\{\begin{array}{l}''CH\\CH_2Et\end{array}\right. \text{ or } \underset{\text{Ethyl-vinyl.}}{\left\{\begin{array}{l}''CH\\CH_2\\CH_2\\CH_3\end{array}\right.}$$

Methyl-allyl differs from ethyl-vinyl.

Character.—The lower members of this series of dyad radicals are gaseous, the higher solid, and the intermediate ones liquid.

The following list includes the known dyad radicals of this series, together with their fusing- and boiling-points :—

		Fusing-point.	Boiling-point.
Ethylene	C_2H_4	——	—
Propylene	C_3H_6	——	−17°·8
Pseudobutylene	C_4H_8	——	− 7·0
Isobutylene	C_4H_8	——	− 5·0
Butylene	C_4H_8	——	+ 3·0
Amylene	C_5H_{10}	——	35·0
Hexylene	C_6H_{12}	——	39·0

		Fusing-point.	Boiling-point.
Heptylene or Œnanthylene	C_7H_{14}	——	55·0°
Octylene or Caprylene	C_8H_{16}	——	95·0
Nonylene	C_9H_{18}	——	125
Paramylene	$C_{10}H_{20}$	——	——
Cetene	$C_{16}H_{32}$	——	——
Cerotene	$C_{27}H_{54}$	57°	275
Melene	$C_{30}H_{60}$	62	375.

Reactions.—1. The dyad radicals of this series all unite directly with chlorine, bromine, and iodine, producing compounds which, in the case of ethylene, are represented by

$$\begin{array}{ccc} \left\{\begin{matrix} CH_2Cl \\ CH_2Cl \end{matrix}\right. & \left\{\begin{matrix} CH_2Br \\ CH_2Br \end{matrix}\right. & \left\{\begin{matrix} CH_2I \\ CH_2I \end{matrix}\right. \\ \text{Ethylenic dichloride.} & \text{Ethylenic dibromide.} & \text{Ethylenic diiodide.} \end{array}$$

These compounds, when treated with alcoholic solution of potassic hydrate, lose one molecule of a hydracid, thus:—

$$\begin{array}{ccccccccc} \left\{\begin{matrix} CH_2Cl \\ CH_2Cl \end{matrix}\right. & + & KHo & = & KCl & + & \left\{\begin{matrix} ''CH \\ CH_2Cl \end{matrix}\right. & + & OH_2. \\ \text{Ethylenic dichloride.} & & \text{Potassic hydrate.} & & \text{Potassic chloride.} & & \text{Vinylic chloride, or chlorinated ethylidene.} & & \text{Water.} \end{array}$$

The monochlorinated radical thus obtained again unites with two atoms of chlorine, producing chlorinated ethylidenic dichloride,

$$\left\{\begin{matrix} CHClCl \\ CH_2Cl \end{matrix}\right. ,$$

which, by further treatment with alcoholic potash, yields dichlorinated ethylidene; and so, by alternate treatments with chlorine and potassic hydrate, ethylene becomes transformed into tetrachlorinated ethylidene. The following formulæ show the first, intermediate, and final compounds:—

$$'' \left\{\begin{matrix} CH_2 \\ CH_2 \end{matrix}\right. \quad \left\{\begin{matrix} CH_2Cl \\ CH_2Cl \end{matrix}\right. \quad \left\{\begin{matrix} ''CH \\ CH_2Cl \end{matrix}\right. \quad \left\{\begin{matrix} CHClCl \\ CH_2Cl \end{matrix}\right. \quad \left\{\begin{matrix} CHClCl \\ ''CH \end{matrix}\right.$$

$$\left\{\begin{matrix} CHClCl \\ CHClCl \end{matrix}\right. \quad \left\{\begin{matrix} ''CCl \\ CHCl_2 \end{matrix}\right. \quad \left\{\begin{matrix} CClCl_2 \\ CHClCl \end{matrix}\right. \quad \left\{\begin{matrix} CCl_3 \\ ''CCl \end{matrix}\right. \cdot$$

Tetrachlorinated ethylidene absorbs two additional atoms of chlorine, producing the solid dicarbonic hexachloride:—

$$\underset{\text{Dicarbonic hexachloride.}}{\left\{\begin{matrix}CCl_3\\CCl_3\end{matrix}\right.}.$$

2. The dyad radicals of the ethylene series can be transformed into the monad radicals from which they are derived If ethylene be digested with hydriodic acid for 50 hours at 100° C., it is transformed into ethylic iodide:—

$$\underset{\text{Ethylene.}}{{}''\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Ethylic iodide.}}{\left\{\begin{matrix}CH_3\\CH_2I\end{matrix}\right.}\cdot$$

From this, ethyl may be prepared, as shown at p. 12.

Isomerism of ethylene and ethylidene compounds.—The chlorides of the dyad radicals are isomeric:—

1. With the chlorides of the monochlorinated normal monad radicals.

2. With the chlorides derived from the aldehydes, which, however, are identical with the chlorides of the monochlorinated normal monad radicals:—

$$\underset{\text{Ethylenic dichloride.}}{\left\{\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right.} \qquad \underset{\text{Ethylidenic dichloride (obtained from aldehyde.)}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.} \qquad \underset{\text{Monochlorinated ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.}\cdot$$

These substances, when treated with alcoholic potash, all yield the same vinylic chloride:—

$$\underset{\text{Ethylenic dichloride.}}{\left\{\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Vinylic chloride.}}{\left\{\begin{matrix}''CH\\CH_2Cl\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic chloride.}}{KCl}.$$

$$\underset{\text{Monochlorinated ethylic chloride, or Ethylidenic dichloride.}}{\left\{\begin{matrix}CH_3\\CHCl_2\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Vinylic chloride.}}{\left\{\begin{matrix}''CH\\CH_2Cl\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic chloride.}}{KCl}.$$

But certain compounds of ethylene yield paralactic acid, whilst the corresponding compounds of ethylidene give lactic acid. The boiling-points of their chlorides also differ, ethylenic dichloride boiling at 85°, whilst ethylidenic dichloride boils at 64°; on the other hand, ethylenic oxide boils at 13°·5, whilst ethylidenic oxide (aldehyde) boils at 20°.

The oxides of the dyad radicals are isomeric :—

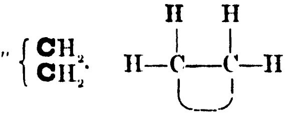
1. With the corresponding aldehydes.

2. With the alcohols of the vinylic or $C_nH_{2n-1}Ho$ series.

The nature of this isomerism is seen from the following formulæ :—

$$\underset{\text{Ethylenic oxide.}}{\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.O} \qquad \underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} \qquad \underset{\text{Vinylic alcohol.}}{\left\{\begin{array}{l}''CH\\CH_2Ho\end{array}\right.}\cdot$$

ETHYLENE.



$$''\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.. \qquad H-\overset{\displaystyle H}{\overset{|}{C}}-\overset{\displaystyle H}{\overset{|}{C}}-H$$

Molecular weight =28. *Molecular volume* ☐☐. 1 *litre weighs* 14 *criths.*

Preparation.—See general methods (p. 16).

Reactions.—1. Decomposed into carbon and marsh-gas by passing through a red-hot tube :—

$$\underset{\text{Ethylene.}}{''\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.} = \underset{\text{Marsh-gas.}}{CH_4} + C.$$

2. Burns in chlorine with deposition of carbon :—

$$\underset{\text{Ethylene.}}{''\left\{\begin{array}{l}CH_2\\CH_2\end{array}\right.} + 2Cl_2 = C_2 + \underset{\text{Hydrochloric acid.}}{4HCl.}$$

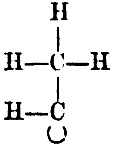
3. Ethylene when agitated with solution of potassic permanganate is oxidized, oxalic acid, formic acid, and carbonic anhydride being formed :—

$$\underset{\text{Ethylene.}}{\mathbf{C}_2H_4} + O_5 = \underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

$$\underset{\text{Ethylene.}}{\mathbf{C}_2H_4} + O_5 = \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Ethylidene, the isomer of ethylene, has not yet been isolated, unless the hydrocarbon C_2H_4 derived from the transformation of ethyl is this body. The constitutional formula of ethylidene is

$$\left\{\begin{matrix}CH_3\\ ''CH\end{matrix}\right..$$



ACETYLENE or C_nH_{2n-2} *SERIES.*

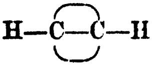
Acetylene is the radical belonging to this series which is best known. The series comprises the following members:—

Acetylene	$\mathbf{C}_2H_2$.
Allylene	$\mathbf{C}_3H_4$.
Crotonylene...........	$\mathbf{C}_4H_6$.
Valerylene	$\mathbf{C}_5H_8$.

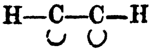
These radicals stand in the same relation to the alcohols of the vinylic series as ethylene bears to ethylic alcohol. They are also probably capable of assuming tetrad functions.

ACETYLENE.

$$'''\mathbf{C}'_2H_2 \text{ or } \left\{\begin{matrix}''\mathbf{C}H\\ ''\mathbf{C}H\end{matrix}\right..$$



or



Molecular weight =26. *Molecular volume* □□. 1 *litre weighs* 13 *criths.*

Preparation.—1. *By synthesis from its elements.* When an electric arc from a moderately powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, acetylene is produced.

2. By the action of water on potassic carbide:—

$$\underset{\text{Potassic carbide.}}{C_2K_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Potassic hydrate.}}{2KHo.}$$

3. By the action of heat upon olefiant gas or the vapour of alcohol, ether, or wood-spirit, or by passing electric sparks through marsh-gas:—

$$\underset{\text{Marsh-gas.}}{2CH_4} = \underset{\text{Acetylene.}}{C_2H_2} + 3H_2.$$

4. By heating the vapour of methylic chloride to low redness:—

$$\underset{\text{Methylic chloride.}}{2CH_3Cl} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + H_2.$$

5. By passing the vapour of chloroform over ignited copper:—

$$\underset{\text{Chloroform.}}{2CHCl_3} + Cu_6 = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Cuprous chloride.}}{3'Cu'_2Cl_2.}$$

6. By the action of calcic carbide upon water:—

$$\underset{\text{Calcic carbide.}}{C_2Ca''} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Calcic hydrate.}}{CaHo_2.}$$

7. From vinylic bromide, one of the derivatives of ethylene, acetylene may be obtained by the action of alcoholic potash:—

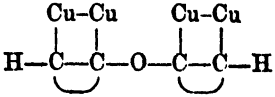
$$\underset{\text{Vinylic bromide.}}{C_2H_3Br} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Potassic bromide.}}{KBr} + \underset{\text{Water.}}{OH_2.}$$

8. By the incomplete combustion of bodies containing carbon and hydrogen:—

$$\underset{\text{Marsh-gas.}}{4CH_4} + 3O_2 = \underset{\text{Acetylene.}}{2C_2H_2} + \underset{\text{Water.}}{6OH_2:}$$

$$\underset{\text{Olefiant gas.}}{2C_2H_4} + O_2 = \underset{\text{Acetylene.}}{2C_2H_2} + \underset{\text{Water.}}{2OH_2.}$$

The crude acetylene, obtained by any of these processes, is best purified by passing it through an ammoniacal solution of cuprous chloride, with which it forms a red precipitate containing $\left\{\begin{array}{l}\mathbf{C}_2'Cu'_2H \\ O \\ \mathbf{C}_2'Cu'_2H\end{array}\right.$.



$$\underset{\text{Cuprous chloride.}}{2'\mathbf{Cu}'_2Cl_2} + \underset{\text{Acetylene.}}{2\mathbf{C}_2H_2} + \mathbf{O}H_2 = \underset{\text{Cuprosovinylic ether. (Acetylide of copper.)}}{\left\{\begin{array}{l}\mathbf{C}_2'Cu'_2H \\ O \\ \mathbf{C}_2'Cu'_2H\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{4HCl.}$$

If ethylene has been present in the crude acetylene, the liquid containing the red precipitate is next heated to boiling, in order to decompose a compound which ethylene forms with copper. The cuprosovinylic ether is then collected upon a filter and washed. On heating cuprosovinylic ether with hydrochloric acid, pure acetylene is evolved:—

$$\underset{\text{Cuprosovinylic ether. (Acetylide of copper.)}}{\left\{\begin{array}{l}\mathbf{C}_2'Cu'_2H \\ O \\ \mathbf{C}_2'Cu'_2H\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Acetylene.}}{2\mathbf{C}_2H_2} + \underset{\text{Cuprous chloride.}}{2'\mathbf{Cu}'_2Cl_2} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

Reactions.—1. When cuprosovinylic ether is heated with zinc and dilute ammonia, the nascent hydrogen, evolved by the action of the zinc upon the ammonia, unites with acetylene, producing ethylene:—

$$\underset{\text{Cuprosovinylic ether.}}{\left\{\begin{array}{l}\mathbf{C}_2'Cu'_2H \\ O \\ \mathbf{C}_2'Cu'_2H\end{array}\right.} + 2H_2 = \underset{\text{Acetylene.}}{2\mathbf{C}_2H_2} + 4Cu + \underset{\text{Water.}}{\mathbf{O}H_2;}$$

$$\underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + H_2 = \underset{\text{Ethylene.}}{\mathbf{C}_2H_4.}$$

2. Acetylene is absorbed by sulphuric acid, producing vinyl-sulphuric acid:—

$$\underset{\text{Acetylene.}}{\mathbf{C}_2H_2} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Vinyl-sulphuric acid.}}{\mathbf{S}O_2(C_2H_3O)Ho.}$$

3. Acetylene unites with bromine, forming acetylenic dibromide :—

$$'''C'_2H_2 + Br_2 = ''C''_2H_2Br_2.$$

Acetylene. Acetylenic dibromide.

4. By agitating acetylene with solution of potassic permanganate, oxalic acid is formed :—

$$'''\left\{\begin{matrix} CH \\ CH \end{matrix}\right. + 2O_2 = \left\{\begin{matrix} COHo \\ COHo \end{matrix}\right.$$

Acetylene. Oxalic acid.

Carbonic anhydride and formic acid are simultaneously produced :—

$$''\left\{\begin{matrix} CH \\ CH \end{matrix}\right. + 2O_2 = \left\{\begin{matrix} H \\ COHo \end{matrix}\right. + CO_2.$$

BROMACETYLENE.

$C_2HBr.$

By boiling together dibromethylenic dibromide with alcoholic potash, a spontaneously inflammable gas is evolved, which is bromacetylene.

$$\left\{\begin{matrix} CHBrBr \\ CHBrBr \end{matrix}\right. = HBr + Br_2 + C_2HBr.$$

Dibromethylenic dibromide. Hydrobromic acid. Bromacetylene.

PHENYLENE or C_nH_{2n-8} *SERIES.*

The dyad radicals of this series are very little known.

The following have alone been isolated :—

Phenylene, C_6H_4.
Toluylene or Stilbene, C_7H_6.

POSITIVE RADICALS.

TRIADS.

These radicals are unknown in the separate state, unless they are identical with the dyad radicals of the acetylene series :—

$$\underset{\text{Acetylene.}}{C_2H_2} = \underset{\text{Formyl.}}{\left\{\begin{matrix}(CH)'''\\(CH)'''\end{matrix}\right.}$$

They are, however, well known in a numerous class of compounds belonging to families which will be studied hereafter.

CHAPTER IV.

ORGANIC RADICALS

Class II.

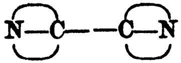
NEGATIVE RADICALS.

Every positive radical may be looked upon as the source of a negative radical, which is generated by displacing a portion of the hydrogen of the former by oxygen. Thus :—

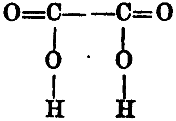
Ethyl	$\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$	yields	acetyl	$\left\{\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right.$
Allyl	$\left\{\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\right.$	„	acryl	$\left\{\begin{matrix}C_3H_3O\\C_3H_3O\end{matrix}\right.$
Ethylene	$(C_2H_4)''$	„	glycolyl	$(C_2H_2O)''$.
Propylene	$(C_3H_6)''$	„	lactyl	$(C_3H_4O)''$.
„		„	malonyl	$(C_3H_2O_2)''$.

The constitution of the so-called compounds of these negative radicals may, however, be more simply explained from another point of view ; and, in fact it will rarely be necessary for us to recognize the existence of more than two negative radicals, in order to understand the whole range of negative organic compounds. These are:—

Cyanogen................ $\left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right.$.



Oxatyl, the molecule of which is dry oxalic acid. $\left\{\begin{matrix} COHo \\ COHo \end{matrix}\right.$.



These two radicals are the acidifying principles of nearly all organic acids; they are, therefore, highly important compounds. The semimolecule of each consists of an atom of carbon, one bond of which is free to combine with other elements or groups of elements, the other three bonds being saturated, in cyanogen by triad nitrogen, and in oxatyl by one atom of oxygen and one semimolecule of hydroxyl. In the molecules of both, the two free bonds of the carbon saturate each other.

These radicals are closely related to each other. Thus, if cyanogen be dissolved in water, it is soon transformed into ammonic oxalate:—

$$\underset{\text{Cyanogen.}}{\left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right.} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Ammonic oxalate.}}{\left\{\begin{matrix} CO(N^vH_4O) \\ CO(N^vH_4O) \end{matrix}\right.}.$$

In the presence of potassic hydrate, cyanogen evolves ammonia and produces potassic oxalate:—

$$\underset{\text{Cyanogen.}}{\left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Potassic oxalate.}}{\left\{\begin{matrix} COKo \\ COKo \end{matrix}\right.} + \underset{\text{Ammonia.}}{2NH_3}.$$

From these salts, oxalic acid, or the molecule of oxatyl, may be readily obtained by the action of sulphuric acid.

In the converse manner, oxatyl may be converted into cyanogen, by transforming it into ammonic oxalate and submitting this salt to the action of heat:—

$$\underset{\text{Ammonic oxalate.}}{\left\{\begin{matrix}CO(N^vH_4O)\\ CO(N^vH_4O)\end{matrix}\right.} = \underset{\text{Water.}}{4OH_2} + \underset{\text{Cyanogen.}}{\left\{\begin{matrix}CN'''\\ CN'''\end{matrix}\right.}$$

CYANOGEN.

in 1815 [illegible]

$$\left\{\begin{matrix}CN'''\\ CN'''\end{matrix}\right. \text{ or } Cy_2.$$

Molecular weight =52 *Molecular volume* ☐☐ 1 *litre weighs* 26 *criths*. *Fuses at* −34°. *Boils at* −20°·7.

[illegible]

Occurrence.—Amongst the gases of blast furnaces,—a proof of its withstanding an extremely high temperature.

Preparation.—By the action of heat on mercuric cyanide:—

$$\underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{HgCy_2} = Hg + \underset{\text{Cyanogen}}{Cy_2.}$$

This equation only partially expresses the reaction, as a brown non-volatile compound (paracyanogen), Cy_n, is simultaneously produced. [illegible]

Reaction.—Cyanogen unites directly with potassium:—

$$\underset{\text{Cyanogen}}{Cy_2} + K_2 = \underset{\substack{\text{Potassic}\\ \text{cyanide.}}}{2KCy.}$$

By passing [illegible]
Coal [illegible]
Cy in [illegible]
combination of Cy [illegible]
[illegible] which is not the [illegible]

HYDROCYANIC ACID.

$$\left\{\begin{matrix}H\\ NC\end{matrix}\right. \text{ or } HCy.$$

Molecular weight =27. *Molecular volume* ☐☐. 1 *litre of hydrocyanic acid vapour weighs* 13·5 *criths*. *Sp. gr. of liquid* 0·7058. *Fuses at* −15°. *Boils at* 26°·5.

[illegible] other has pentad N
C – H and H – N ≡ C, the latter is considered to be the [illegible]

Preparation.—1. In the anhydrous condition, by passing hydrosulphuric acid over mercuric cyanide:—

formed in

10 and

$$\underset{\text{Mercuric cyanide.}}{HgCy_2} + \underset{\text{Sulphuretted hydrogen.}}{SH_2} = \underset{\text{Mercuric sulphide.}}{HgS''} + \underset{\text{Hydrocyanic acid.}}{2HCy.}$$

2. By distilling potassic cyanide, or ferrocyanide, with dilute sulphuric acid:—

$$\underset{\text{Potassic cyanide.}}{2KCy} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Hydrocyanic acid.}}{2HCy} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2.}$$

3. By passing nitrogen over an ignited mixture of potassic carbonate and carbon:—

$$\underset{\text{Potassic carbonate.}}{COKo_2} + C_4 + N_2 = \underset{\text{Potassic cyanide.}}{2KCy} + \underset{\text{Carbonic oxide.}}{3CO.}$$

The potassic cyanide thus formed is then treated according to process No. 2.

4. By heating together an alcoholic solution of ammonia, chloroform, and potassic hydrate:—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Chloroform.}}{CHCl_3} + 3KHo = 3KCl + \underset{\text{Hydrocyanic acid.}}{NCH} + 3OH_2.$$

Reactions.—1. Hydrocyanic acid in contact with water slowly passes, partly into ammonic oxalate as mentioned at p. 26, and partly into ammonic formate:— [illegible] a trace of [illegible] to prepare by (2), it keeps [illegible]

$$\underset{\text{Hydrocyanic acid}}{NCH} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Ammonic formate.}}{\begin{cases} H \\ CO(N^vH_4O). \end{cases}}$$

2. If hydrocyanic acid be mixed with concentrated hydrochloric acid, formic acid and ammonic chloride are produced:—

$$\underset{\text{Hydrocyanic acid.}}{NCH} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Formic acid.}}{\begin{cases} H \\ COHo \end{cases}} + \underset{\text{Ammonic chloride.}}{NH_4Cl.}$$

3. The displacement of the hydrogen in hydrocyanic acid by metals gives rise to a very extensive series of single and double cyanides. The following is a list of the most important of these compounds:—

It is generally very stable

Single Cyanides.

Potassic cyanide	KCy.
Zincic cyanide	$\mathbf{Zn}Cy_2$.
Cadmic cyanide	$\mathbf{Cd}Cy$.
Nickelous cyanide	$\mathbf{Ni}Cy_2$.
Argentic cyanide	$AgCy$.
Mercuric cyanide	$\mathbf{Hg}Cy_2$
Aurous cyanide	$AuCy$.
Cuprous cyanide	$'\mathbf{Cu}'_2Cy_2$.
Ferrous cyanide	$\mathbf{Fe}Cy_2$.
Cobaltous cyanide	$\mathbf{Co}Cy_2$.

Double Cyanides.

Dipotassic zincic tetracyanide	K_2Zn'', Cy_4.
Dipotassic cadmic tetracyanide	K_2Cd'', Cy_4.
Dipotassic nickelous tetracyanide	K_2Ni'', Cy_4.
Potassic argentic dicyanide	KAg, Cy_2.
Potassic aurous dicyanide	KAu, Cy_2.
Potassic auric tetracyanide	KAu''', Cy_4.
Dipotassic cuprous tetracyanide	$K_2'Cu'_2, Cy_4$.
Dipotasssic platinous tetracyanide	K_2Pt'', Cy_4.
Tetrapotassic diplatinic decacyanide	$K_4'Pt'''_2Cy_{10}$.
Tetrapotassic ferrous hexacyanide. (Potassic ferrocyanide.)	$K_4, Fe''Cy_6$.
Hexapotassic diferric dodecacyanide. (Potassic ferricyanide.)	$K_6, 'Fe'''_2Cy_{12}$.
Hexapotassic dicobaltic dodecacyanide. (Potassic cobalticyanide.)	$K_6, 'Co'''_2Cy_{12}$.
Hexapotassic dichromic dodecacyanide	$K_6, 'Cr'''_2Cy_{12}$.
Hexapotassic dimanganic dodecacyanide	$K_6'Mn'''_2, Cy_{12}$.

The cyanides of the alkali metals when fused in contact with air, absorb oxygen, producing cyanates:—

$$\underset{\text{Potassic cyanide.}}{KCy} + O = \underset{\text{Potassic cyanate.}}{CyKo}.$$

Some of the single cyanides, as potassic cyanide, are readily

decomposed by acids; others, as ferrous and aurous cyanides, may be boiled with moderately strong acids without decomposition.

Most of the insoluble single cyanides dissolve in solutions of the alkaline cyanides, forming double cyanides. Some of these double compounds, when acted upon by hydrochloric acid, evolve hydrocyanic acid, producing chlorides of both metals, as in the case of dipotassic zincic tetracyanide. These are called *easily decomposable cyanides*, and are indicated in the above Table by the comma being placed between the cyanogen and the metals.

Other double cyanides do not evolve hydrocyanic acid under the influence of hydrochloric acid, but produce a chloride of one of the metals, the remaining elements of the compound uniting with hydrogen to form a complex acid. In the above Table the double cyanides of this class are indicated by the comma being placed between the metals.

The most important of these double cyanides are the potassic ferrocyanide $K_4,\ Fe''Cy_6$, and the potassic ferricyanide $K_6,\ 'Fe'''_2Cy_{12}$.

POTASSIC FERROCYANIDE.

$K_4,\ Fe''Cy_6$ or K_4Cfy.

Preparation.—1. By placing a mixture of iron filings and solution of potassic cyanide in contact with the air, oxygen is absorbed and potassic ferrocyanide produced:—

$$Fe + \underset{\text{Potassic cyanide.}}{6KCy} + \underset{\text{Water.}}{OH_2} + O = \underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Potassic hydrate.}}{2KHo.}$$

2. By digesting potassic cyanide with ferrous sulphide:—

$$\underset{\text{Ferrous sulphide.}}{FeS''} + \underset{\text{Potassic cyanide.}}{6KCy} = \underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Potassic sulphide.}}{SK_2.}$$

3. On a manufacturing scale it is prepared by fusing nitrogenous animal matter with potassic carbonate and iron filings in

iron vessels, lixiviating the resulting mass with water, and crystallizing.

Reactions.—1. Potassic ferrocyanide, when fused with potassic carbonate, forms potassic cyanide and cyanate:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Potassic carbonate.}}{COKo_2} = \underset{\text{Potassic cyanide}}{5KCy} + \underset{\text{Potassic cyanate.}}{CyKo} + Fe + \underset{\text{Carbonic anhydride}}{CO_2}.$$

2. By mixing solution of potassic ferrocyanide with ether and hydrochloric acid, hydroferrocyanic acid is precipitated:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Hydrochloric acid}}{4HCl} = \underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Hydroferrocyanic acid.}}{Fe''Cy_6H_4}.$$

3. Potassic ferrocyanide produces, with solutions of ferrous salts, a light-blue precipitate, which rapidly becomes dark blue in contact with the air:—

$$\underset{\text{Potassic ferrocyanide.}}{Fe''Cy_6K_4} + \underset{\text{Ferrous sulphate}}{SO_2Feo''} = \underset{\text{Light-blue precipitate.}}{Fe''Cy_6Fe''K_2} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2}.$$

4. With ferric salts it gives prussian blue:—

$$\underset{\text{Potassic ferrocyanide.}}{3Fe''Cy_6K_4} + \underset{\text{Ferric chloride.}}{2Fe_2Cl_6} = \underset{\text{Prussian blue.}}{3Fe''Cy_2, 2'Fe'''_2Cy_6} + \underset{\text{Potassic chloride}}{12KCl}.$$

5. With cupric salts it gives a red precipitate of cupric ferrocyanide:—

$$\underset{\text{Potassic ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Cupric sulphate}}{2SO_2Cuo''} = \underset{\text{Cupric ferrocyanide.}}{Cu''_2Fe''Cy_6} + \underset{\text{Potassic sulphate.}}{2SO_2Ko_2}.$$

POTASSIC FERRICYANIDE.

$K_6, 'Fe'''_2Cy_{12}$ or K_3Cfdy.

Preparation.—By the action of oxidizing substances, such as chlorine or nitric acid, on potassic ferrocyanide:—

$$\underset{\text{Potassic ferrocyanide.}}{2K_4Fe''Cy_6} + Cl_2 = \underset{\text{Potassic ferricyanide.}}{K_6'Fe'''_2Cy_{12}} + \underset{\text{Potassic chloride.}}{2KCl}.$$

Reaction.—Potassic ferricyanide produces no precipitate with solutions of ferric salts, but causes a deep-blue precipitate with ferrous compounds:—

$K_6{}'Fe'''_2Cy_{12}$	+	$3SO_2Feo''$	=	$Fe''_3{}'Fe'''_2Cy_{12}$	+	$3SO_2Ko_2$.
Potassic ferricyanide		Ferrous sulphate		Turnbull's blue.		Potassic sulphate.

[illegible] OTHER COMPOUNDS OF CYANOGEN.

There are three isomeric chlorides of cyanogen:—

$CyCl$.	Cy_2Cl_2 [illegible]	Cy_3Cl_3. [illegible]
Gaseous	Liquid.	Solid

The molecular volume of all three cyanic chlorides is ☐☐.

1 *litre of gaseous cyanic chloride weighs*	30·75	*criths.*
1 *litre of vapour of liquid cyanic chloride weighs*	61·5	„
1 *litre of vapour of solid cyanic chloride weighs*	92·25	„

Cyanogen produces, with hydroxyl, three isomeric acids and an isomeric neutral body:—

Cyanic acid	$CyOH$ or $CyHo$.
Cyanuric acid	$Cy_3O_3H_3$ or Cy_3Ho_3.
Fulminuric acid	$Cy_3O_3H_3$ or Cy_3Ho_3.
Cyamelide	$Cy_nO_nH_n$ or Cy_nHo_n.

When potassic cyanide is boiled with sulphur, the latter is dissolved and the solution contains potassic sulphocyanate:—

CyK	+	S	=	$CyKs$.
Potassic cyanide				Potassic sulphocyanate

This compound produces with ferric salts a blood-red colour.

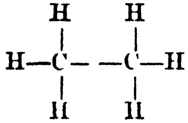
[illegible]

OXATYL.

$$\left\{\begin{array}{l}COHo\\COHo\end{array}\right.$$

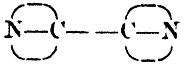
This radical, in the isolated condition, constitutes dry oxalic acid; and in combination with hydrogen and other radicals it enters into the composition of nearly all organic acids. Acids containing one semimolecule of oxatyl are monobasic, those containing two are dibasic, and those containing three are tribasic.

The relations between methyl, oxatyl, and cyanogen are very simple:—



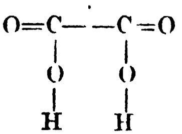
$\left\{\begin{matrix}\mathbf{C}H_3\\\mathbf{C}H_3\end{matrix}\right.$.

Methyl.



$\left\{\begin{matrix}\mathbf{C}N'''\\\mathbf{C}N'''\end{matrix}\right.$.

Cyanogen.



$\left\{\begin{matrix}\mathbf{C}OHo\\\mathbf{C}OHo\end{matrix}\right.$.

Oxatyl.

In methyl the two carbon atoms are united together by one bond of each, the remaining three bonds of each atom being saturated by three atoms of hydrogen. In cyanogen the carbon atoms are united in the same manner, but the three remaining bonds of each carbon atom are saturated by triad nitrogen; whilst in oxatyl the three remaining bonds are saturated with the dyad element oxygen and the monad radical hydroxyl.

Oxatyl has not been united with chlorine to produce oxatylic chloride ($\mathbf{C}OHoCl$); nor has its hydroxyl been replaced by chlorine to form $\left\{\begin{matrix}\mathbf{C}OCl\\\mathbf{C}OCl\end{matrix}\right.$. When treated with phosphoric chloride, it yields carbonic oxide and carbonic anhydride:—

$$\underset{\text{Oxatyl.}}{\left\{\begin{matrix}\mathbf{C}OHo\\\mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Phosphoric chloride.}}{\mathbf{P}Cl_5} = \underset{\text{Carbonic oxide}}{\mathbf{C}O} + \underset{\text{Carbonic anhydride}}{\mathbf{C}O_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Phosphoric oxytrichloride.}}{\mathbf{P}OCl_3}.$$

OXALIC ACID.

$$\left\{\begin{matrix}\mathbf{C}OHo\\\mathbf{C}OHo\end{matrix}\right., 2\mathbf{O}H_2 \text{ (crystallized).}$$

Occurrence.—In the form of the hydric potassic salt in *Oxalis acetosella*, and in the form of different salts in many other plants, and also in the animal organism.

Preparation.—1. From its elements through the medium of potassic cyanide. (See pp. 26 & 28.)

2. By passing carbonic anhydride over heated sodium:—

$$\underset{\text{Carbonic anhydride}}{2\mathbf{C}O_2} + Na_2 = \underset{\text{Sodic oxalate.}}{\left\{\begin{matrix}\mathbf{C}ONao\\\mathbf{C}ONao\end{matrix}\right.}$$

3. By the oxidation of a large number of organic compounds. Most organic substances are converted by oxidizing agents into oxalic acid before their final transformation into carbonic anhydride and water: thus sugar is transformed into oxalic acid by the action of nitric acid.

4. By heating sawdust with a mixture of potash and soda, oxalates of these bases are formed.

Transformations.—1. By the action of heat, oxalic acid is transformed into carbonic anhydride and oxatylic hydride, or formic acid:—

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathbf{C}OHo\\\mathbf{C}OHo\end{matrix}\right.} = \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\\mathbf{C}OHo\end{matrix}\right.}$$

A portion of the formic acid is at the same time decomposed into water and carbonic oxide:—

$$\underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\\mathbf{C}OHo\end{matrix}\right.} = \underset{\text{Water.}}{\mathbf{O}H_2} + \underset{\text{Carbonic oxide.}}{\mathbf{C}O.}$$

2. Substances having a strong attraction for water, such as sul-

phuric acid, transform oxalic acid into water, carbonic oxide, and carbonic anhydride:—

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\substack{\text{Carbonic}\\ \text{oxide.}}}{\mathrm{CO}} + \underset{\substack{\text{Carbonic}\\ \text{anhydride}}}{\mathrm{CO_2}} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

3. Heated with an excess of alkali, oxalic acid (or an oxalate) yields hydrogen and a carbonate:—

$$\underset{\substack{\text{Potassic}\\ \text{oxalate.}}}{\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COKo}\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2\mathrm{KHo}} = \underset{\substack{\text{Potassic}\\ \text{carbonate}}}{2\mathrm{COKo_2}} + \mathrm{H_2}.$$

4. Argentic oxalate explodes when heated, producing silver and carbonic anhydride:—

$$\underset{\substack{\text{Argentic}\\ \text{oxalate.}}}{\left\{\begin{matrix}\mathrm{COAgo}\\ \mathrm{COAgo}\end{matrix}\right.} = \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{2\mathrm{CO_2}} + \mathrm{Ag_2}.$$

Salts of Oxalic acid.—Oxalic acid forms three series of salts:—

Normal.	Acid.	Superacid.
$\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COKo}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COKo}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COKo}\end{matrix}\right.$ $\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.$
$\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right.\mathrm{Bao''}.$	$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{CO}\\ \mathrm{Bao''}\\ \mathrm{CO}\\ \mathrm{COHo}\end{matrix}\right..$	

OXAMIC ACID.

$$\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{COAd}\\ \mathrm{COHo}\end{matrix}\right.$$

Preparation.—By heating hydric ammonic oxalate to 230°:—

$$\underset{\substack{\text{Hydric ammonic}\\ \text{oxalate.}}}{\left\{\begin{matrix}\mathrm{CO(N^{v}H_4O)}\\ \mathrm{COHo}\end{matrix}\right.} = \underset{\text{Oxamic acid.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Reaction.—**By boiling oxamic acid with water it is retransformed into hydric ammonic oxalate.**

OXAMIDE.

$$\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\ \mathbf{C}O(N'''H_2)\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathbf{C}OAd\\ \mathbf{C}OAd\end{matrix}\right..$$

Preparation.—1. By distilling normal ammonic oxalate:—

$$\underset{\text{Normal ammonic oxalate.}}{\left\{\begin{matrix}\mathbf{C}O(N^{v}H_4O)\\ \mathbf{C}O(N^{v}H_4O)\end{matrix}\right.} = \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\ \mathbf{C}O(N'''H_2)\end{matrix}\right.}.$$

2. By acting upon ethylic oxalate by ammonia:—

$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{matrix}\mathbf{C}OEto\\ \mathbf{C}OEto\end{matrix}\right.} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\ \mathbf{C}O(N'''H_2)\end{matrix}\right.} + \underset{\text{Alcohol.}}{2EtHo}.$$

Reactions.—1. Oxamide, when heated with phosphoric anhydride, evolves cyanogen:—

$$\underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\ \mathbf{C}O(N'''H_2)\end{matrix}\right.} = \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Cyanogen.}}{\left\{\begin{matrix}\mathbf{C}N'''\\ \mathbf{C}N'''\end{matrix}\right.}.$$

2. Dilute acids convert it into oxalic acid and ammonic salts:—

$$\underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\ \mathbf{C}O(N'''H_2)\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.}$$

$$+ \underset{\text{Ammonic sulphate.}}{\mathbf{S}O_2(N^{v}H_4O)_2}.$$

By distilling the oxalates of the compound ammonias instead of ammonic oxalate, compound oxamides are obtained:—

$$\underset{\text{Methylammonic oxalate.}}{\left\{\begin{matrix}\mathbf{C}O(N^{v}MeH_3O)\\ \mathbf{C}O(N^{v}MeH_3O)\end{matrix}\right.} = \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Dimethyloxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''MeH)\\ \mathbf{C}O(N'''MeH)\end{matrix}\right.}.$$

$$\underset{\text{Phenylammonic oxalate.}}{\left\{\begin{matrix}\mathbf{C}O(N^{v}PhH_3O)\\ \mathbf{C}O(N^{v}PhH_3O)\end{matrix}\right.} = \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Diphenyloxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''PhH)\\ \mathbf{C}O(N'''PhH)\end{matrix}\right.}.$$

CHAPTER V.

HYDRIDES OF THE ORGANIC RADICALS.

This family is divided into two classes :—

Class I. Hydrides of the Positive Radicals.
Class II. Hydrides of the Negative Radicals.

Class I.

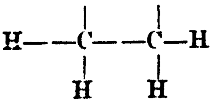
HYDRIDES OF THE POSITIVE RADICALS.

Two series of hydrides belonging to this class are well known, they are:—

1. Hydrides of the Radicals of the Methyl series.
2. Hydrides of the Radicals of the Phenyl series.

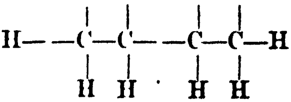
1. *HYDRIDES OF THE RADICALS OF THE METHYL SERIES, Marsh-gas or* C_nH_{2n+2} *Series.*

There is some difference of opinion as to whether these compounds are identical or isomeric with the radicals of the methyl series. Thus methyl and ethylic hydride both contain C_2H_6, and ethyl and butylic hydride both contain C_4H_{10}. The graphic formulæ exhibit no difference between these pairs of bodies respectively. Thus:—



$$\begin{array}{ccccc} & a & \mathrm{H} & b & \mathrm{H} & \\ & & | & & | & \\ \mathrm{H}— & & —\mathrm{C}— & & —\mathrm{C}— & \mathrm{H} \\ & & | & & | & \\ & & \mathrm{H} & & \mathrm{H} & \end{array}$$

Methyl or ethylic hydride.



$$\begin{array}{cccccccc} & c & \mathrm{H} & \mathrm{H} & d & \mathrm{H} & \mathrm{H} & \\ & & | & | & & | & | & \\ \mathrm{H}— & & —\mathrm{C}— & \mathrm{C}— & & —\mathrm{C}— & \mathrm{C}— & \mathrm{H} \\ & & | & | & & | & | & \\ & & \mathrm{H} & \mathrm{H} & & \mathrm{H} & \mathrm{H} & \end{array}$$

Ethyl or butylic hydride.

These formulæ do not show us whether the molecule of methyl or ethylic hydride will separate at *a* and so be represented by the formula $\left\{\begin{matrix}C(CH_3)H_2\\H\end{matrix}\right.$, or at *b* and so be written thus,

$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_3\end{matrix}\right.$; or whether the molecule of ethyl or butylic hydride will separate at *c*, and so be formulated $\left\{\begin{matrix}\mathbf{C}(C_3H_7)H_2\\ H\end{matrix}\right.$—or at *d*, when it should be represented by $\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}(CH_3)H_2\end{matrix}\right.$. Some experiments in connexion with this subject appear to show that these compounds are isomeric.

A difference between methyl and ethylic hydride can only be conceived on the supposition that the four bonds of carbon have not equal values in combination, an hypothesis which is not altogether unsupported by facts.

Preparation.—1. There is only one process of general application for preparing these hydrides; it consists in bringing water into contact with the zinc compounds of the respective radicals:—

$$\underset{\text{Zinc compound of radical.}}{\mathbf{Zn}(C_nH_{2n+1})_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2} + \underset{\text{Hydride of radical.}}{2\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.}.$$

The corresponding compounds containing more positive metals might doubtless be substituted for those of zinc.

2. There are several special processes which may be used for preparing these hydrides. Thus all the hydrides above that of methyl may be obtained, together with the corresponding dyad radical, by acting upon the iodide of the monad radical by zinc:—

$$\underset{\text{Iodide of the monad radical.}}{2\left\{\begin{matrix}C_nH_{2n+1}\\ I\end{matrix}\right.} + Zn = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Dyad radical.}}{C_nH_{2n}} + \underset{\text{Hydride of monad radical.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ H\end{matrix}\right.}.$$

Methylic hydride, or marsh-gas, is produced during putrefaction, and by the distillation of potassic acetate with excess of potassic hydrate.

The destructive distillation of coal and of allied substances also furnishes a large number of the members of this series.

Character.—They are all distinguished by their great chemical indifference, and by their forming substitution compounds containing chlorine, bromine, &c.

The following list contains the hydrides of the monad radicals hitherto studied:—

Methylic hydride, or Marsh-gas	MeH	or $C\ H_4$	
Ethylic hydride	EtH	or C_2H_6	
Propylic or tritylic hydride	PrH	or C_3H_8	
Butylic or tetrylic hydride	BuH	or C_4H_{10}	slightly above 0°
Amylic or pentylic hydride	AyH	or C_5H_{12}	30°
Hexylic or caproylic hydride	CpH	or C_6H_{14}	68°
Heptylic hydride		C_7H_{16}	92- 94°
Octylic hydride		C_8H_{18}	116–118°
Nonylic hydride		C_9H_{20}	136 138°
Decatylic hydride		$C_{10}H_{22}$	160-162°
Endecatylic hydride		$C_{11}H_{24}$	180 184°
Dodecatylic hydride		$C_{12}H_{26}$	196-200°
Tridecatylic hydride		$C_{13}H_{28}$	216 218°
Tetradecatylic hydride		$C_{14}H_{30}$	236–240°
Pentadecatylic hydride		$C_{15}H_{32}$	255-260°

METHYLIC HYDRIDE, *Marsh-gas, Light Carburetted Hydrogen, Fire-damp.*

CH_4 or MeH.

Molecular weight = 16. *Molecular volume* ☐☐. 1 *litre weighs* 8 *criths.*

Occurrence.—1. As a product of the decomposition of organic substances out of contact with air.

2. Evolved in coal-mines.

3. The gas of the mud-volcano at Bulganak in the Crimea is nearly pure marsh-gas.

Preparation.—1. By the action of water on zincic methide. (See general reaction, p. 38.)

2. By distilling two parts of potassic acetate, two of potassic hydrate, and three of lime:—

$$\underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Potassic carbonate.}}{COKo_2} + \underset{\text{Methylic hydride.}}{CH_4}.$$

3. By the reduction of carbonic chloride or of chloroform with sodium amalgam and water:—

$$\underset{\text{Carbonic chloride.}}{\mathbf{C}Cl_4} + H_8 = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Methylic hydride.}}{\mathbf{C}H_4}:$$

$$\underset{\text{Chloroform.}}{\mathbf{C}HCl_3} + H_6 = \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Methylic hydride.}}{\mathbf{C}H_4}.$$

4. By passing carbonic disulphide and hydrosulphuric acid, or carbonic disulphide and steam, over ignited copper:—

$$\underset{\text{Carbonic disulphide.}}{\mathbf{C}S''_2} + \underset{\text{Sulphuretted hydrogen.}}{2\mathbf{S}H_2} + 4Cu = \underset{\text{Cupric sulphide.}}{4\mathbf{Cu}S''} + \underset{\text{Methylic hydride.}}{\mathbf{C}H_4}.$$

5. By the destructive distillation of organic substances, such as wood and coal.

Reactions.—1. When equal volumes of methylic hydride and chlorine are exposed to diffused daylight, methylic chloride is formed:—

$$\underset{\text{Methylic hydride.}}{\mathbf{C}H_4} + Cl_2 = \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Methylic chloride.}}{\mathbf{C}H_3Cl}.$$

2. When methylic hydride is passed through a red-hot tube, hydrogen, ethylene, acetylene, and ethylic hydride are produced.

ETHYLIC HYDRIDE.

$\mathbf{C}_2H_6$ or $\mathbf{C}MeH_3$.

Molecular weight =30. *Molecular volume* ☐☐. 1 *litre weighs* 15 *criths.*

Preparation.—1. By the action of water on zincic ethide (see p. 38).

2. By the action of ethylic iodide on sodic ethide, ethylene being simultaneously produced:—

$$\underset{\text{Sodic ethide.}}{\mathbf{C}MeH_2Na} + \underset{\text{Ethylic iodide.}}{\mathbf{C}MeH_2I} = \underset{\text{Sodic iodide.}}{NaI} + \underset{\text{Ethylene.}}{\mathbf{C}_2H_4} + \underset{\text{Ethylic hydride.}}{\mathbf{C}MeH_3}.$$

Reactions.—1. When equal volumes of ethylic hydride and chlorine are exposed to diffused daylight, the following action takes place:—

$$\underset{\text{Ethylic hydride.}}{\mathbf{C}\mathrm{MeH_3}} + \mathrm{Cl_2} = \underset{\beta\text{ Ethylic chloride.}}{\mathbf{C}\mathrm{MeH_2Cl}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

A small portion of the body $\mathbf{C}\mathrm{MeH_2Cl}$ is ordinary ethylic chloride, which is a liquid, boiling at 12°·5; but the rest is a gas which does not condense at −18°.

2. When a mixture of two volumes of chlorine and one of ethylic hydride is exposed to the action of diffused daylight, an oily liquid having the composition of ethylenic dichloride is formed:—

$$\underset{\text{Ethylic hydride.}}{\mathbf{C}\mathrm{MeH_3}} + 2\mathrm{Cl_2} = \mathbf{C}_2\mathrm{H_4Cl_2} + \underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}}.$$

AMYLIC HYDRIDE.

$\mathbf{C}_5\mathrm{H}_{12}$ or $\mathbf{C}\mathrm{BuH_3}$.

Molecular weight = 72. *Molecular volume* $\square\square$. 1 *litre of amylic hydride vapour weighs* 36 *criths. Boils at* 30°.

Occurrence.—In petroleum and coal-oil.

Preparation.—By digesting zinc and amylic iodide with water or alcohol at 100°:—

$$\underset{\text{Amylic iodide.}}{2\mathbf{C}\mathrm{BuH_2I}} + 2\mathrm{Zn} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H_2}} = \underset{\text{Amylic hydride.}}{2\mathbf{C}\mathrm{BuH_3}}$$

$$+ \underset{\text{Zincic hydrate.}}{\mathbf{Zn}\mathrm{Ho_2}} + \underset{\text{Zincic iodide.}}{\mathbf{Zn}\mathrm{I_2}}.$$

PARAFFIN.

$\mathrm{C_nH_{2n+2}}$.

This body is produced, together with numerous other compounds of a like nature, by the destructive distillation of boghead coal and similar substances. It is also found in petroleum and asphalt. Chlorine has no action upon paraffin in the cold; but if it be passed into melted paraffin, the latter is slowly attacked, hydrochloric acid being evolved. In this reaction paraffin resembles the hydrides of the monad radicals, and differs from the dyad radicals, to which class it was formerly considered to belong. In the formula C_nH_{2n+2} for paraffin, the value of *n* has not yet been satisfactorily determined; in fact it is probable that several distinct hydrides of the class now under consideration are confounded under this name.

2. *HYDRIDES OF THE RADICALS OF THE PHENYL SERIES.*

The following six members of this series are known, viz.:—

	Formulæ.	Boiling-points. °	Sp. gr.
Pentol	C_5H_4	60·0	——
Benzol	C_6H_6	80·5	0·85
Toluol.......	C_7H_8	110·0	0·87
Xylol	C_8H_{10}	128·5	——
Cumol	C_9H_{12}	148·5	0·87
Cymol	$C_{10}H_{14}$	171·4	0·86

Preparation.—1. These hydrides are produced by the distillation of the alkaline salts of the acids containing the same positive radicals, with excess of potassic hydrate:—

$$\underset{\text{Potassic salt.}}{\left\{\begin{matrix} C_nH_{2n-7} \\ COKo \end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Potassic carbonate.}}{COKo_2} + \underset{\text{Hydride of radical.}}{\left\{\begin{matrix} C_nH_{2n-7} \\ H \end{matrix}\right.}.$$

2. By the destructive distillation of various organic substances, such as coal.

Methyl-phenyl, C_6H_5Me, is ordinary coal-tar toluol.

Ethyl-phenyl, C_6H_5Et, is not xylol from coal-tar; it boils at 135°, six or seven degrees above the boiling-point of coal-tar xylol. Ethyl-phenyl produces a nitro-compound which can be distilled; it boils at 233°. Ethyl-phenyl, when oxidized by chromic acid, gives benzoic acid and carbonic anhydride, while xylol gives terephthalic acid.

Xylol from coal-tar is dimethyl-benzol or methyl-benzyl, $\mathbf{C}_6H_4Me_2$. It may be produced by the action of bromotoluol upon methylic iodide in presence of sodium.

Diethyl-benzol, by oxidation with chromic acid, gives water, carbonic anhydride, and terephthalic acid:—

$$\underset{\text{Diethyl benzol.}}{\mathbf{C}_6H_4Et_2} + 12O = \underset{\text{Terephthalic acid.}}{\mathbf{C}_6H_4(COHo)_2} + 2\mathbf{C}O_2 + 4\mathbf{O}H_2.$$

Oxidized with dilute nitric acid, it gives ethylbenzoic acid:—

$$\underset{\text{Diethyl-benzol.}}{\mathbf{C}_6H_4Et_2} + 6O = \underset{\text{Ethyl-benzoic acid}}{\mathbf{C}_6H_4Et(COHo)} + \mathbf{C}O_2 + 2\mathbf{O}H_2.$$

Cymol from cumin oil and from camphor are isomeric.

Methyl-xylol or trimethyl-benzol, $\mathbf{C}_6H_3Me_3$, is the cumol of tar. It boils at 165°–166°, and gives a compound with bromine fusing at 72°–73°.

Ethyl-xylol, dimethyl ethyl-benzol, $\mathbf{C}_6H_3Me_2Et$, boils at 183°–184°, and by oxidation gives acetic acid and an acid resembling terephthalic.

Properties.—These hydrides are distinguished from those of the radicals of the C_nH_{2n+1} series by being less indifferent to chemical agents. By treatment with strong nitric acid they yield nitro-compounds:—

Thus Pentol, $\mathbf{C}_5H_4$, gives nitropentol, $\mathbf{C}_5H_3(N^vO_2)$?
„ Benzol, $\mathbf{C}_6H_6$, „ nitrobenzol, $\mathbf{C}_6H_5(N^vO_2)$.
„ Toluol, $\mathbf{C}_7H_8$, „ nitrotoluol, $\mathbf{C}_7H_7(N^vO_2)$.
„ Xylol, $\mathbf{C}_8H_{10}$, „ nitroxylol, $\mathbf{C}_8H_9(N^vO_2)$.
„ Cumol, $\mathbf{C}_9H_{12}$, „ nitrocumol, $\mathbf{C}_9H_{11}(N^vO_2)$.
„ Cymol, $\mathbf{C}_{10}H_{14}$, „ nitrocymol, $\mathbf{C}_{10}H_{13}(N^vO_2)$.

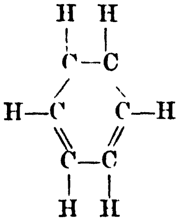
Under the influence of reducing agents, these nitro-compounds yield aniline and its homologues.

Pure nitrotoluol is solid at ordinary temperatures. It boils at 287°. By reduction it gives toluidine; and by the action of potassic chromate and sulphuric acid, paranitrobenzoic acid or nitrodracylic acid is formed.

So-called liquid nitrotoluol is a mixture of nitrobenzol and nitrotoluol.

BENZOL, *Benzene*, *Benzine*, *Phenylic Hydride*, *Bicarburet of Hydrogen*.

C_6H_6 or PhH.



Molecular weight =78. *Molecular volume* ☐☐. 1 *litre of benzol-vapour weighs* 39 *criths*. *Fuses at* 5°·5. *Boils at* 80°·5.

Occurrence.—In Rangoon petroleum and in coal-tar.

Preparation.—1. By heating benzoic acid with excess of lime or baryta:—

$$\underset{\text{Benzoic acid.}}{\left\{\begin{matrix} C_6H_5 \\ COHo \end{matrix}\right.} + \underset{\text{Lime.}}{CaO} = \underset{\text{Benzol.}}{\left\{\begin{matrix} C_6H_5 \\ H \end{matrix}\right.} + \underset{\text{Calcic carbonate.}}{COCao''}.$$

2. By heating the vapour of benzoic acid to redness, when it splits into benzol and carbonic anhydride:—

$$\underset{\text{Benzoic acid.}}{\left\{\begin{matrix} C_6H_5 \\ COHo \end{matrix}\right.} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Benzol.}}{C_6H_6}.$$

3. By heating phthalic acid with lime:—

$$\underset{\text{Phthalic acid.}}{C_8H_6O_4} + \underset{\text{Lime.}}{2\mathbf{C}aO} = \underset{\text{Benzol.}}{\mathbf{C}_6H_6} + \underset{\text{Calcic carbonate.}}{2\mathbf{C}OCao''}.$$

4. By passing fats through red-hot tubes.

5. By the destructive distillation of coal.

6. In small quantity, when the vapour of acetic acid or of alcohol is passed through a red-hot tube.

SUBSTITUTION DERIVATIVES OF BENZOL.

I. *Bromo-Compounds.*

MONOBROMBENZOL.

$\mathbf{C}_6H_5Br$.

Boils at 150°.

Preparation.—By acting with two atoms of bromine on boiling benzol:—

$$\underset{\text{Benzol.}}{\mathbf{C}_6H_6} + Br_2 = \underset{\text{Monobrombenzol or phenylic bromide.}}{\mathbf{C}_6H_5Br} + \underset{\text{Hydrobromic acid.}}{HBr}.$$

DIBROMBENZOL.

$\mathbf{C}_6H_4Br_2$.

Fuses at 89°. ***Boils at*** 219°.

Preparation.—By treating monobrombenzol with excess of bromine.

TRIBROMBENZOL HYDROBROMATE.

$\mathbf{C}_6H_6Br_6$.

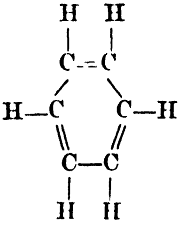
Preparation.—By exposing a mixture of benzol and bromine to the action of sunlight.

TRIBROMBENZOL.

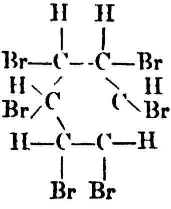
$C_6H_3Br_3$.

Preparation.—By boiling the previous compound with alcoholic potash.

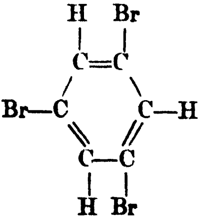
The following graphic formulæ show the probable atomic relations subsisting between benzol, tribrombenzol hydrobromate, and tribrombenzol:—



Benzol.



Tribrombenzol hydrobromate.



Tribrombenzol.

II. *Chloro-compounds.*

Benzol forms three chloro- substitution compounds, similar to the bromo-compounds just described.

		State of aggregation.	Fusing-point.	Boiling-point	Sp. gr.
Monochlorbenzol ..	$\mathbf{C}_6H_5Cl$,	Liquid ..	——	136°.	——
Dichlorbenzol ..	$\mathbf{C}_6H_4Cl_2$,	Solid ...	89°.	——	——
Trichlorbenzol	$\mathbf{C}_6H_3Cl_3$,	Oily ..	——	210°	1·457.

III. *Nitro-compounds.*

Two only have hitherto been produced:—

Nitrobenzol	$\mathbf{C}_6H_5(N^{v}O_2)$ or $\mathbf{N}(C_6H_5)O_2$.
Dinitrobenzol .	$\mathbf{C}_6H_4(N^{v}O_2)_2$ or $\mathbf{N}_2(C_6H_4)''O_4$.

NITROBENZOL.

$\mathbf{N}(C_6H_5)O_2$ or $\mathbf{N}PhO_2$.

Molecular weight =123. *Molecular volume* $\square\!\square$. 1 *litre of nitrobenzol vapour weighs* 61 5 *criths. Fuses at* 3°. *Boils at* 220°.

Preparation.—By the action of nitric acid on benzol:—

$$\underset{\text{Benzol.}}{\mathbf{C}_6H_6} + \underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} = \underset{\text{Nitrobenzol.}}{\mathbf{N}(C_6H_5)O_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Reactions.—1. By the action of reducing or hydrogenating agents, as zinc and hydrochloric acid, sulphuretted hydrogen, acetic acid and iron, or potassic arsenite, nitrobenzol is converted into aniline:—

$$\mathbf{N}(C_6H_5)O_2 + 3\mathbf{S}H_2 = \mathbf{N}(C_6H_5)H_2 + 2\mathbf{O}H_2 + S_3$$

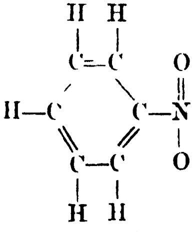
$$\text{or } \underset{\text{Nitrobenzol.}}{\mathbf{C}_6H_5(N^{v}O_2)} + \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}H_2} = \underset{\text{Aniline.}}{\mathbf{C}_6H_5(N'''H_2)} + \underset{\text{Water.}}{2\mathbf{O}H_2} + S_3.$$

2. Nitrobenzol is also converted into aniline when its

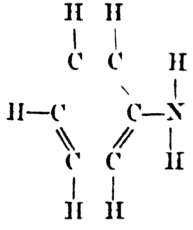
vapour, mixed with hydrogen, is passed over spongy palladium:—

$$\underset{\text{Nitrobenzol.}}{\mathbf{N}(C_6H_5)O_2} + 3H_2 = \underset{\text{Aniline.}}{\mathbf{N}(C_6H_5)H_2} + \underset{\text{Water.}}{2\mathbf{O}H_2}$$

The relation between nitrobenzol and aniline will be seen in the following graphic formulæ:—



Nitrobenzol.



Aniline.

3. By the action of sodium amalgam and water, nitrobenzol is converted into azobenzol, and finally into hydrazobenzid:—

$$\underset{\text{Nitrobenzol.}}{2\mathbf{N}(C_6H_5)O_2} + H_8 = \underset{\text{Azobenzol.}}{\begin{Bmatrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}(C_6H_5)\end{Bmatrix}} + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

$$\underset{\text{Azobenzo}}{\begin{Bmatrix}\mathbf{N}(C_6H_5)\\ \mathbf{N}(C_6H_5)\end{Bmatrix}} + H_2 = \underset{\text{Hydrazobenzid.}}{\begin{Bmatrix}\mathbf{N}(C_6H_5)H\\ \mathbf{N}(C_6H_5)H\end{Bmatrix}}.$$

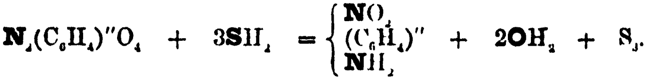
DINITROBENZOL.

$N_2(C_6H_4)''O_4$.

Fuses below 100°.

Preparation.—By treating nitrobenzol with a mixture of concentrated nitric and sulphuric acids.

Reaction.—By the action of sulphuretted hydrogen, dinitrobenzol is converted into nitraniline:—



$$\underset{\text{Dinitrobenzol.}}{N_2(C_6H_4)''O_4} + \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{3SH_2} = \underset{\text{Nitraniline.}}{\left\{\begin{matrix} NO_2 \\ (C_6H_4)'' \\ NH_2 \end{matrix}\right.} + \underset{\text{Water.}}{2OH_2} + S_3.$$

CLASS II.

HYDRIDES OF NEGATIVE RADICALS.

Only two of these are known:—

Cyanic hydride or Hydrocyanic acid.
Oxatylic hydride or Formic acid.

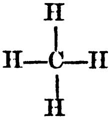
The first has already been considered (p. 27); and the second will be more conveniently studied in connexion with the fatty acids (p. 121).

CHAPTER VI.

THE ALCOHOLS.

THE alcohols form one of the most important of the families of organic compounds. The simplest member of this family is methylic alcohol, which is derived from marsh-gas by the substitution of one semimolecule of hydroxyl for one of hydrogen.

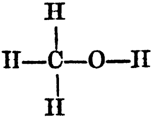
CH_4.



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Marsh-gas.

CH_3Ho.



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

Methylic alcohol.

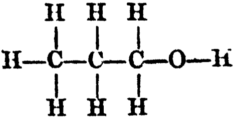
The alcohols have been termed the hydrated oxides of the positive radicals; but this is eroneous, as they do not contain water. They may more correctly be defined as the compounds of hydroxyl with the positive organic radicals, whence it follows that each series of positive radicals forms a corresponding series of alcohols. The alcohols act upon and saturate acids, forming a family of compounds termed *ethereal salts*. The acidity or acid-saturating power of the alcohols depends upon the number of semimolecules of hydroxyl which they contain: the monad radicals give monohydric alcohols, or alcohols containing only one semimolecule of hydroxyl, the dyad radicals dihydric alcohols, &c. We have thus the annexed three principal subdivisions of the alcohol family.

Monohydric.	Dihydric.	Trihydric.
Methyl or $C_nH_{2n+1}Ho$ series.	Glycol or $C_nH_{2n}Ho_2$ series.	Glycerin or $C_nH_{2n-1}Ho_3$ series.
Vinyl or $C_nH_{2n-1}Ho$ series.	Orcin or $C_nH_{2n-8}Ho_2$ series.	Pyrogallic or $C_nH_{2n-9}Ho_3$ series.
Phenyl or $C_nH_{2n-7}Ho$ series.		

The following symbolic and graphic formulæ will exemplify the disposal of the bonds in these three subdivisions:—

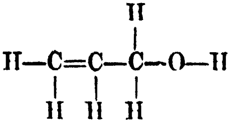
Monohydric Alcohols.

Propylic alcohol. (*Methyl series.*) $= C_3H_7Ho$ or $\left\{\begin{array}{l} C(CH_3)H_2 \\ CH_2Ho \end{array}\right.$.



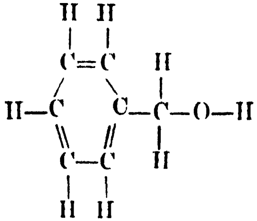
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - O - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Allylic alcohol. (*Vinyl series.*) = $\mathbf{C}_3H_5Ho$ or $\left\{\begin{array}{l}\mathbf{C}(CH_2)''H \\ \mathbf{C}H_2Ho\end{array}\right.$.



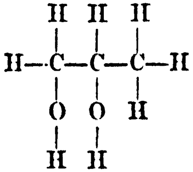
$$\begin{array}{ccccccccccc} & & & & & & H & & & & \\ & & & & & & | & & & & \\ H & - & C & = & C & - & C & - & O & - & H \\ & & | & & | & & | & & & & \\ & & H & & H & & H & & & & \end{array}$$

Benzoic alcohol. (*Phenyl series.*) = $\mathbf{C}_7H_7Ho$ or $\left\{\begin{array}{l}\mathbf{C}_6H_5 \\ \mathbf{C}H_2Ho\end{array}\right.$.



Dihydric Alcohols.

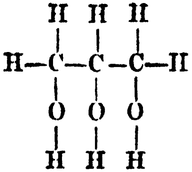
Propylenic alcohol, or propylic glycol .... = $\mathbf{C}_3H_6Ho_2$ or $\left\{\begin{array}{l}\mathbf{C}(CH_3)HHo \\ \mathbf{C}H_2Ho\end{array}\right.$.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & O & & H & & \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Trihydric Alcohols.

Glycerin .... = $\mathbf{C}_3H_5Ho_3$ or $\left\{\begin{array}{l}\mathbf{C}H_2Ho \\ \mathbf{C}HHo \\ \mathbf{C}H_2Ho\end{array}\right.$.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & O & & O & & \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

MONOHYDRIC ALCOHOLS:

Methyl or $C_nH_{2n+1}Ho$ series.

These alcohols may be divided into three classes, viz.:—

1. Monohydric normal alcohols $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$.

2. „ secondary „ $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_mH_{2m+1})HHo\end{matrix}\right.$.

3. „ tertiary „ $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}(C_mH_{2m+1})_2Ho\end{matrix}\right.$.

In the general formula of the normal alcohols *n* may $=0$, and even the whole radical $\mathbf{C}(C_nH_{2n+1})H_2$ may be replaced by hydrogen, as is the case in methylic alcohol. In the formulæ of the secondary and tertiary alcohols *n* may also $=0$, but *m* must always be a positive integer.

NORMAL MONOHYDRIC ALCOHOLS.

General formula $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$.

The following is a list of the members of this class:—

		Fusing-points.	Boiling-points.
Methylic alcohol	$\left\{\begin{matrix}H\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	66°·5.
Ethylic alcohol	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	78°·4.
Propylic or tritylic alcohol	$\left\{\begin{matrix}\mathbf{C}MeH_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	97°.
Butylic or tetrylic alcohol	$\left\{\begin{matrix}\mathbf{C}EtH_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_2H_5)H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	115°.
Isobutylic alcohol	$\left\{\begin{matrix}\mathbf{C}Me_2H\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(CH_3)_2H\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	109°.
Amylic or pentylic alcohol	$\left\{\begin{matrix}\mathbf{C}PrH_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_3H_7)H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	137°.
Isamylic alcohol	$\left\{\begin{matrix}\mathbf{C}Pr\beta H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(\mathbf{C}Me_2H)H_2\\ \mathbf{C}H_2Ho\end{matrix}\right.$	−20°.	129°.
Pseudamylic alcohol	$\left\{\begin{matrix}\mathbf{C}EtMeH\\ \mathbf{C}H_2Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(C_2H_5)(CH_3)H\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	128°.
Caproylic or hexylic alcohol	$\left\{\begin{matrix}\mathbf{C}_5H_{11}\\ \mathbf{C}H_2Ho\end{matrix}\right.$	—	150°.

		Fusing-points.	Boiling-points.
Œnanthylic or heptylic alcohol………	$\left\{\begin{matrix}C_6H_{13}\\CH_2Ho\end{matrix}\right.$	——	170°.
Caprylic or octylic alcohol……………	$\left\{\begin{matrix}C_7H_{15}\\CH_2Ho\end{matrix}\right.$	——	190°.
Nonylic alcohol ………………………	$\left\{\begin{matrix}C_8H_{17}\\CH_2Ho\end{matrix}\right.$	——	200°.
Decatylic alcohol………………………	$\left\{\begin{matrix}C_9H_{19}\\CH_2Ho\end{matrix}\right.$	——	212°.
Cetylic alcohol ……………… ……	$\left\{\begin{matrix}C_{15}H_{31}\\CH_2Ho\end{matrix}\right.$	50°.	——
Cerotic alcohol ……………… ……	$\left\{\begin{matrix}C_{26}H_{53}\\CH_2Ho\end{matrix}\right.$	79°.	——
Melissic alcohol …… …………………	$\left\{\begin{matrix}C_{29}H_{59}\\CH_2Ho\end{matrix}\right.$	85°.	——

The lower members of the class are liquid, and the higher solid. They are produced in a variety of operations, such as destructive distillation, fermentation, and animal secretion, but by reactions which cannot usually be traced.

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the monad* C_nH_{2n+1} *radicals.*

1. The radicals C_nH_{2n+1} which are combined with hydroxyl in the normal alcohols may be separated, by first converting the alcohol into an iodide (see p. 96), and subsequently acting on the iodide by zinc (see p. 11).

2. The radical next lower in the series, than that contained in the alcohol, may be obtained by converting the alcohol into the corresponding fatty acid, and then submitting a salt of this acid to electrolysis (see p. 119).

3. Inversely, the normal alcohols may be obtained by acting upon the normal radicals with chlorine under the influence of light, when one atom of hydrogen in the radical is displaced by chlorine.

Thus in the case of methyl we have

$$\underset{\text{Methyl.}}{\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.} + Cl_2 = \underset{\text{Chlorinated methyl.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}:$$

by the action of potassic hydrate upon this chlorinated methyl, ethylic alcohol is formed, thus:—

$$\underset{\text{Chlorinated methyl.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

This reaction requires further investigation (see p. 55).

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the dyad* C_nH_{2n} *radicals.*

1. The C_nH_{2n} radicals are obtained from the normal $C_nH_{2n+1}Ho$ alcohols by the abstraction of the elements of water:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} - \underset{\text{Water.}}{OH_2} = \underset{\text{Ethylene.}}{{}^{\prime\prime}\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.}.$$

2. Inversely, the normal alcohols are obtained from these radicals by first uniting the latter with hydrochloric, hydrobromic, or hydriodic acid, and then treating the product with potassic hydrate:—

$$\underset{\text{Ethylene.}}{{}^{\prime\prime}\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.}$$

$$\underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}CH_3\\CH_2Cl\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

Or by uniting the dyad radicals with sulphuric acid, and distilling the product with water:—

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Ethylene.}}{C_2H_4} = \underset{\text{Sulphovinic acid.}}{SO_2Ho(C_2H_5O)}:$$

$$\underset{\text{Sulphovinic acid.}}{SO_2EtoHo} + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Ethylic alcohol.}}{EtHo.}$$

Relations of the normal $C_nH_{2n+1}Ho$ *alcohols to the hydrides of the* C_nH_{2n+1} *radicals.*

1. When the alcohols are converted into iodides (see p. 36) and the latter digested with zinc and water at 100°, the corresponding hydrides are produced (see p. 38).

2. When the hydrides of the C_nH_{2n+1} radicals are acted upon by chlorine under the influence of light, they produce the chlorides of the radicals, from which the alcohols may be obtained by the action of potassic hydrate:—

$$\underset{\substack{\text{Ethylic}\\\text{hydride.}}}{EtH} + Cl_2 = \underset{\substack{\text{Ethylic}\\\text{chloride.}}}{EtCl} + \underset{\substack{\text{Hydrochlo-}\\\text{ric acid.}}}{HCl};$$

$$\underset{\substack{\text{Ethylic}\\\text{chloride.}}}{EtCl} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{EtHo} + \underset{\substack{\text{Potassic}\\\text{chloride}}}{KCl}.$$

The greater quantity of the chlorine compound so formed is isomeric with the chloride of the radical, and possibly gives a corresponding isomeric alcohol.

Relations of the $C_nH_{2n+1}Ho$ *alcohols to the radical cyanogen. Ascent of the alcohol series. Mendius's reaction.*

By the dry distillation of potassic sulphovinate and its homologues with potassic cyanide, the nitriles or abnormal cyanides of the radicals are produced:—

$$\underset{\substack{\text{Potassic}\\\text{sulphovinate.}}}{\mathbf{S}O_2EtoKo} + \underset{\substack{\text{Potassic}\\\text{cyanide.}}}{KCy} = \underset{\substack{\text{Potassic}\\\text{sulphate.}}}{\mathbf{S}O_2Ko_2} + \underset{\substack{\text{Ethylic}\\\text{nitrile.}}}{EtCy}.$$

By treatment with nascent hydrogen, this ethylic nitrile is converted into propylamine:—

$$\underset{\text{Ethylic nitrile.}}{\mathbf{N}C(\mathbf{C}MeH_2)} + H_4 = \underset{\text{Propylamine.}}{\mathbf{N}[\mathbf{C}(\mathbf{C}MeH_2)H_2]H_2 \text{ or } \mathbf{N}PrH_2}.$$

By the action of nitrous anhydride, propylamine is transformed into isopropylic alcohol :—

$$\underset{\text{Propylamine.}}{2NPrH_2} + \underset{\text{Nitrous anhydride.}}{N_2O_3} = \underset{\text{Isopropylic alcohol.}}{2\beta PrHo} + \underset{\text{Water.}}{OH_2} + 2N_2.$$

It is obvious that by repeating these reactions on isopropylic alcohol, butylic alcohol would be obtained, the homologous series of alcohols being ascended one step at each repetition of the process. But the alcohols are, if possible, secondary or tertiary.

METHYLIC ALCOHOL, *Wood Spirit, Pyroxylic Spirit.*

CH_3Ho or $MeHo$.

Molecular weight =32. *Molecular volume* $\square\square$. 1 *litre of methylic alcohol vapour weighs* 16 *criths. Sp. gr.* 0·798. *Boils at* 66°·5.

Preparation.—1. From marsh-gas, by the action of chlorine and subsequent treatment with potassic hydrate :—

$$\underset{\text{Marsh-gas.}}{CH_4} + Cl_2 = \underset{\text{Methylic chloride}}{CH_3Cl} + \underset{\text{Hydrochloric acid.}}{HCl};$$

$$\underset{\text{Methylic chloride.}}{CH_3Cl} + \underset{\text{Potassic hydrate}}{KHo} = \underset{\text{Methylic alcohol.}}{CH_3Ho} + \underset{\text{Potassic chloride.}}{KCl}.$$

2. From the essential oil of *Gaultheria procumbens*, by the action of potassic hydrate :—

$$\underset{\text{Oil of \textit{Gaultheria procumbens}. (Methosalicylic acid.)}}{C_7H_4OMeoHo} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Potassic salicylate.}}{C_7H_4OHoKo} + \underset{\text{Methylic alcohol.}}{MeHo}.$$

3. By the destructive distillation of wood.

Reactions.—1. Methylic alcohol unites with some salts in the capacity of water of crystallization, as, for instance,—

$$CaCl_2, 2MeHo.$$

2. By the action of potassium and sodium, methylates are formed with elimination of hydrogen :—

$$\underset{\text{Potassic}}{CH_3Ko}. \qquad \underset{\text{Sodic methylate.}}{CH_3Nao}.$$

3. By oxidation it is transformed into formic acid:—

$$\underset{\substack{\text{Methylic}\\\text{alcohol.}}}{\left\{\begin{matrix}\mathrm{H}\\\mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\\mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

4. When distilled with calcic chloro-hypochlorite (*chloride of lime*) and water, chloroform is produced.

$$\underset{\substack{\text{Methylic}\\\text{alcohol.}}}{2\mathrm{CH_3Ho}} + \underset{\substack{\text{Calcic chloro-}\\\text{hypochlorite.}}}{4\mathrm{Ca(OCl)Cl}} = \underset{\text{Chloroform.}}{2\mathrm{CHCl_3}} + \underset{\substack{\text{Calcic oxy-}\\\text{chloride.}}}{\left\{\begin{matrix}\mathrm{CaCl}\\\mathrm{O}\\\mathrm{Ca''}\\\mathrm{O}\\\mathrm{Ca''}\\\mathrm{O}\\\mathrm{CaCl}\end{matrix}\right.} + \underset{\text{Water.}}{3\mathrm{OH_2}}.$$

ETHYLIC ALCOHOL, *Alcohol, Spirit of Wine.*

$$\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2Ho}\end{matrix}\right. \text{ or } \mathrm{EtHo}.$$

Molecular weight = 46. *Molecular volume* □□. 1 *litre of ethylic alcohol vapour weighs* 23 *criths.* *Sp. gr.* 0·792 *at* 20°. *Boils at* 78°·4.

Preparation.—1. From ethylene (p. 54).

2. By the fermentation of grape-sugar with yeast at a temperature of about 22°:—

$$\underset{\text{Grape-sugar.}}{\mathrm{C_6H_{12}O_6}} = \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{2\mathrm{C_2H_5Ho}} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{2\mathrm{CO_2}}.$$

At the same time, however, other products are formed, but in very small quantities.

Reactions.—1. Treated with potassium or sodium, alcohol forms ethylates:—

$$\underset{\text{Potassic}}{\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2Ko}\end{matrix}\right.} \qquad \underset{\text{Sodic ethylate.}}{\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2Nao}\end{matrix}\right.}$$

2. When passed through a red-hot tube, alcohol is decomposed into marsh-gas, hydrogen, and carbonic oxide:—

$$\underset{\text{Ethylic alcohol.}}{\mathbf{C}_2H_5Ho} = \underset{\text{Marsh-gas.}}{\mathbf{C}H_4} + H_2 + \underset{\text{Carbonic oxide.}}{\mathbf{C}O}.$$

Small quantities of ethylene, benzol, and naphthalin are simultaneously produced, whilst carbon is deposited.

3. By oxidation, ethylic alcohol is converted first into aldehyde, and then into acetic acid:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right.} + O = \underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OH\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OH\end{matrix}\right.} + O = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.}$$

4. Distilled with chloride of lime, ethylic alcohol produces chloroform.

Alcoholates are salts containing alcohol in the place of water of crystallization; they are mostly decomposed immediately by water.

The following are known:—

$$\mathbf{Zn}Cl_2, 2\mathbf{C}_2H_5Ho.$$
$$\mathbf{Ca}Cl_2, 4\mathbf{C}_2H_5Ho.$$
$$\mathbf{N}_2O_4Mgo'', 6\mathbf{C}_2H_5Ho.$$

5. Treated with chlorine as long as hydrochloric acid is evolved, it is transformed into ethylic chloride and chloral hydrate (the aldehyde of trichloracetic acid):—

$$2\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{matrix}\right.} + 4Cl_2 = \underset{\text{Chloral hydrate.}}{\left\{\begin{matrix}\mathbf{C}Cl_3\\ \mathbf{C}HHo_2\end{matrix}\right.} + \underset{\text{Ethylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}H_2Cl\end{matrix}\right.} + 4HCl.$$

MERCAPTAN, *Sulphur Alcohol, Ethylic sulphhydrate, Hydrosulphate of Ethyl.*

$$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Hs}\end{array}\right. \text{ or } \mathrm{EtHs}.$$

Molecular weight = 62. *Molecular volume* $\square\!\square$. 1 *litre of mercaptan vapour weighs* 31 *criths. Sp. gr. of liquid* 0·835. *Boils at* 63°.

Preparation.—By distilling potassic sulphovinate with potassic sulphhydrate:—

$$\begin{array}{ccccccc}\mathrm{SO_2EtoKo} & + & \mathrm{KHs} & = & \mathrm{EtHs} & + & \mathrm{SO_2Ko_2}.\\ \text{Potassic sulphovinate.} & & \text{Potassic sulphhydrate.} & & \text{Mercaptan.} & & \text{Potassic sulphate.}\end{array}$$

Reactions.—1. By the action of potassium and sodium on mercaptan, an atom of hydrogen is displaced by the metal, producing mercaptides:—

$$\begin{array}{ccc}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Ks}\end{array}\right. & \qquad & \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Nas}\end{array}\right.\\ \text{Potassic mercaptide.} & & \text{Sodic mercaptide}\end{array}$$

2. Mercaptan acts upon mercuric oxide with great energy, a white crystalline mercuric mercaptide being formed:—

$$\begin{array}{ccccccc}2\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Hs}\end{array}\right. & + & \mathrm{HgO} & = & \begin{array}{l}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2}\end{array}\right.\\ \left\{\begin{array}{l}\mathrm{CH_2}\\ \mathrm{CH_3}\end{array}\right.\end{array}\mathrm{Hgs''} & + & \mathrm{OH_2}.\\ \text{Mercaptan} & & \text{Mercuric oxide.} & & \text{Mercuric mercaptide.} & & \text{Water.}\end{array}$$

Propylic alcohol, $\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{CH_2Ho}\end{array}\right.$, is obtained from the fusel oil of the marc brandy of the south of France.

Butylic alcohol, $\left\{\begin{array}{l}\mathrm{CMe_2H}\\ \mathrm{CH_2Ho}\end{array}\right.$, is contained in the fusel oil produced in the preparation of spirit from the molasses of beet-root sugar. Butylic alcohol of the form $\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{CH_2Ho}\end{array}\right.$ is obtained from butylic acid by Piria and Wurtz's reactions, described at p. 120.

Amylic alcohol, $\left\{\begin{array}{l}\mathbf{C}\mathrm{Pr}\beta\mathrm{H}_2\\ \mathbf{C}\mathrm{H}_2\mathrm{Ho}\end{array}\right.$, *is the chief constituent of the fusel oil obtained in the manufacture of alcohol from potatoes or grain.* Two other normal, isomeric amylic alcohols are given in the Table at p. 52.

As far as these alcohols have been studied, they resemble, in their chemical relations, the two previously described.

SECONDARY MONOHYDRIC ALCOHOLS.

General formula... $\left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})\mathrm{H}_2\\ \mathbf{C}(\mathrm{C}_m\mathrm{H}_{2m+1})\mathrm{HHo}\end{array}\right.$

The secondary alcohols differ from the normal in yielding, by oxidation, ketones instead of acids.

Seven secondary alcohols are at present known:—

		Boiling-points. °
Isopropylic alcohol or dimethyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{MeHHo}\end{array}\right.$	84.
Methylethyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{EtHHo}\end{array}\right.$	97.
Methylpropyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{PrHHo}\end{array}\right.$	122.
Methylisopropyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Me}_2\mathrm{H}\\ \mathbf{C}\mathrm{MeHHo}\end{array}\right.$	106.
Pseudohexylic alcohol or methylbutyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{PrH}_2\\ \mathbf{C}\mathrm{MeHHo}\end{array}\right.$	136.
Methylhexyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}(\mathrm{C}_6\mathrm{H}_{13})\mathrm{HHo}\end{array}\right.$	184.
Methylnonyl carbinol	$\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}(\mathrm{C}_9\mathrm{H}_{19})\mathrm{HHo}\end{array}\right.$	229.

The first is obtained by the action of nascent hydrogen on acetone:—

$$\underset{\text{Acetone.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OMe}\end{array}\right.} + \mathrm{H}_2 = \underset{\text{Isopropylic alcohol.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{MeHHo}\end{array}\right.}$$

The relation existing between ethylic alcohol, propylic alcohol, and isopropylic alcohol, will at once be evident from the following formulæ:—

$$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{C(CH_3)H_2}\\ \mathrm{CH_2Ho}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{C(CH_3)HHo}\end{array}\right.$$

Ethylic alcohol. Propylic alcohol. Isopropylic alcohol.

From these formulæ it is seen that propylic alcohol is ethylic alcohol in which one atom of hydrogen in the methyl (or *non-oxygenated* part of the compound) is displaced by methyl; whereas isopropylic alcohol is ethylic alcohol in which one atom of hydrogen in the *oxygenated* part of the compound is displaced by methyl.

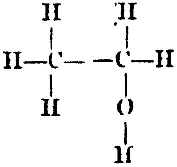
Ethylic alcohol boils at ...	78°·4
Propylic alcohol „ ...	97
Isopropylic alcohol „ ...	84

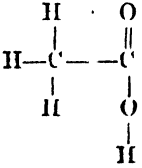
Thus, by substituting an atom of methyl for one of hydrogen in the non-oxygenated part of the alcohol, the addition of CH_2 raises the boiling-point 18°·6; whilst, if an atom of hydrogen in the oxygenated part be similarly displaced, the same addition only raises the boiling-point 5°·6.

Isopropylic alcohol yields by oxidation a ketone, and not an acid. The radical oxatyl being a necessary constituent in organic acids, it will be seen from the following equations that, although propylic alcohol can be converted into an acid without the disruption of its carbon atoms, isopropylic alcohol cannot be so transformed:—

$$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Ho}\end{array}\right. + \mathrm{O_2} = \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COHo}\end{array}\right. + \mathrm{OH_2}.$$

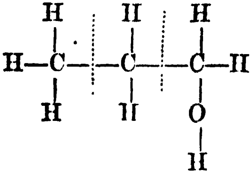
Ethylic alcohol. Acetic acid. Water.

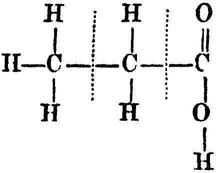




$$\left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}H_2Ho\end{matrix}\right. + O_2 = \left\{\begin{matrix}\mathbf{C}(CH_3)H_2\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{O}H_2.$$

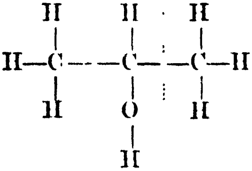
Propylic alcohol. Propionic acid. Water.

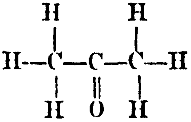




$$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}(CH_3)HHo\end{matrix}\right. + O = \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O(CH_3)\end{matrix}\right. + OH_2.$$

Isopropylic alcohol. Acetone. Water.





TERTIARY MONOHYDRIC ALCOHOLS.

General formula...... $\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})H_3\\ \mathbf{C}(C_mH_{2m+1})_2Ho\end{matrix}\right.$.

The following members of this series are known :—

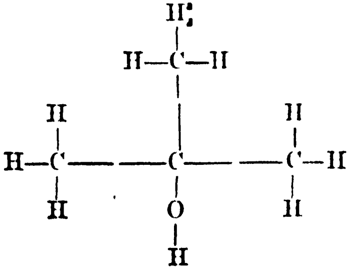
		Boiling-points.
Pseudobutylic alcohol or trimethyl carbinol	$\mathbf{C}Me_3Ho$	82°·5.
Dimethylethyl carbinol ...	$\mathbf{C}EtMe_2Ho$	100°.
Dimethylpropyl carbinol	$\mathbf{C}PrMe_2Ho$	120°.
Dimethylisopropyl carbinol	$\mathbf{C}\beta PrMe_2Ho$	112°.
Methyldiethyl carbinol ...	$\mathbf{C}Et_2MeHo$	115°.
Triethyl carbinol	$\mathbf{C}Et_3Ho$	141°.
Diethylpropyl carbinol ...	$\mathbf{C}PrEt_2Ho$	——

Pseudobutylic alcohol, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}Me_2Ho\end{matrix}\right.$, exists in small quantities in butylic alcohol obtained by fermentation; it has also been produced by acting with zincic methide on acetylic chloride, and submitting the product thus obtained to the action of water:—

$$\underset{\text{Acetylic chloride.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OCl\end{matrix}\right.} + \underset{\text{Zincic methide.}}{2\mathbf{Zn}Me_2} = \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}Me_2(Zn''MeO)\end{matrix}\right. + \underset{\text{Zincic chlormethide.}}{\mathbf{Zn}MeCl};$$

$$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}Me_2(Zn''MeO)\end{matrix}\right. + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Pseudobutylic alcohol.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}Me_2Ho\end{matrix}\right.}$$

$$+ \underset{\text{Methylic hydride.}}{\mathbf{C}H_4} + \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2}.$$



or $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}(CH_3)_2Ho\end{matrix}\right.$

Pseudobutylic alcohol.

CHAPTER VII.

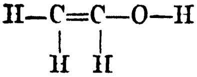
MONOHYDRIC ALCOHOLS:

Vinyl or $C_nH_{2n-1}Ho$ series.

Two alcohols only of this series are known; of these the first is a secondary, and the second a normal alcohol:

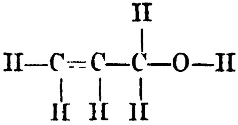
$$\text{Vinylic alcohol...}'' \left\{ \begin{array}{l} CH_2 \\ CHHo \end{array} \right. \quad \text{or} \quad CMe''HHo.$$

$$\text{Allylic alcohol ...} \left\{ \begin{array}{l} CMe''H \\ CH_2Ho \end{array} \right. .$$



$$H{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}{-}O{-}H$$

Vinylic alcohol.



$$H{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}O{-}H$$

Allylic alcohol.

VINYLIC ALCOHOL.

$$'' \left\{ \begin{array}{l} CH_2 \\ CHHo \end{array} \right. ?$$

Preparation.—By combining acetylene with sulphuric acid and distilling the product with water, in the same manner as in the preparation of ethylic alcohol from ethylene (p. 54):—

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Acetylene.}}{C_2H_2} = \underset{\text{Sulphovinylic acid.}}{SO_2(C_2H_3O)Ho.}$$

$$\underset{\text{Sulphovinylic acid.}}{SO_2(C_2H_3O)Ho} + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Vinylic alcohol.}}{CMe''HHo.}$$

This alcohol is isomeric with aldehyde and with ethylenic oxide:—

$$\underset{\text{Vinylic alcohol.}}{'' \left\{ \begin{array}{l} CH_2 \\ CHHo \end{array} \right.} \qquad \underset{\text{Aldehyde.}}{\left\{ \begin{array}{l} CH_3 \\ COH \end{array} \right.} \qquad \underset{\text{Ethylenic oxide.}}{\left\{ \begin{array}{l} CH_2 \\ CH_2 \end{array} \right. O.}$$

If the above, and not $\left\{ \begin{array}{l} ''CH \\ CH_2Ho \end{array} \right.$, be the vinylic alcohol from acetylene, it is obvious that this body could not yield an acid by oxidation; but if the latter formula represents it, this alcohol is normal and ought to yield on oxidation an acid, $\left\{ \begin{array}{l} ''CH \\ COHo \end{array} \right.$, homologous with acrylic acid.

ALLYLIC ALCOHOL.

$$\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{CH_2Ho}\end{matrix}\right. \text{ or All Ho.}$$

Boils at 96°·5. *Sp. gr. of liquid at* 0°=0·8709.

Preparation.—Glycerin, when submitted to the action of diphosphorous tetriodide, yields allylic iodide:—

$$\underset{\text{Diphosphorous tetriodide.}}{'\mathrm{P''_2I_4}} + \underset{\text{Glycerin.}}{2\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CHHo}\\ \mathrm{CH_2Ho}\end{matrix}\right.} = \underset{\text{Allylic iodide.}}{2''\left\{\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH}\\ \mathrm{CH_2I}\end{matrix}\right.} + \underset{\text{Phosphorous acid.}}{2\mathrm{POHHo_2}} + \mathrm{I_2}.$$

The allylic iodide is then decomposed by argentic oxalate, when allylic oxalate is formed:—

$$\underset{\text{Allylic iodide.}}{2\mathrm{AllI}} + \underset{\text{Argentic oxalate.}}{\left\{\begin{matrix}\mathrm{COAgo}\\ \mathrm{COAgo}\end{matrix}\right.} = \underset{\text{Allylic oxalate.}}{\left\{\begin{matrix}\mathrm{COAllo}\\ \mathrm{COAllo}\end{matrix}\right.} + \underset{\text{Argentic iodide.}}{2\mathrm{AgI}}.$$

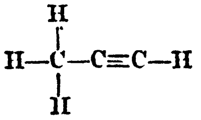
The allylic oxalate is next decomposed by ammonia, when oxamide and allylic alcohol are produced:—

$$\underset{\text{Allylic oxalate.}}{\left\{\begin{matrix}\mathrm{COAllo}\\ \mathrm{COAllo}\end{matrix}\right.} + \underset{\text{Ammonia.}}{2\mathrm{NH_3}} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathrm{CO(N'''H_2)}\\ \mathrm{CO(N'''H_2)}\end{matrix}\right.} + \underset{\text{Allylic alcohol.}}{2\mathrm{AllHo}}.$$

Reactions.—1. In all ordinary reactions, allylic alcohol behaves like ethylic alcohol. By oxidation it gives acrylic acid:—

$$\underset{\text{Allylic alcohol.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \mathrm{O_2} = \underset{\text{Acrylic acid.}}{\left\{\begin{matrix}\mathrm{CMe''H}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

2. With phosphoric anhydride it yields allylene:—



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}C{\equiv}C{-}H} = '''\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{C}\\ \mathrm{CH}\end{matrix}\right..$$

Among the ethereal salts of allylic alcohol, the sulphide and sulphocyanate occur in nature as garlic and mustard oils:—

$$\left\{\begin{array}{l}CMe''H\\CH_2\\S''\\CH_2\\CMe''H\end{array}\right. . \qquad ''\left\{\begin{array}{l}CMe''H\\CH_2\\N\\CS''\end{array}\right. .$$

Allylic sulphide. (Garlic oil.)

Allylic sulphocyanate. (Mustard oil.)

CHAPTER VIII.

MONOHYDRIC ALCOHOLS:

Phenyl or C_nH_{2n-7} series.

These alcohols may be divided into a normal and a tertiary class. The members of the first class possess the general character of the normal alcohols of the ethyl series, while those of the second class exhibit a slightly acid character.

Class I. Normal Alcohols.

General formula............ $\left\{\begin{array}{l}C_nH_{2n-7}\\CH_2Ho\end{array}\right. .$

Benzylic alcohol* .... $\left\{\begin{array}{l}C_6H_5\\CH_2Ho\end{array}\right. .$

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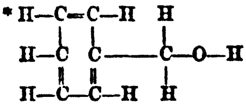

Xylylic alcohol .... $\left\{\begin{array}{l}C_6MeH_4\\CH_2Ho\end{array}\right.$

Cumylic alcohol .... $\left\{\begin{array}{l}C_9H_{11}\\CH_2Ho\end{array}\right.$

Sycocerylic alcohol .... $\left\{\begin{array}{l}C_{17}H_{27}\\CH_2Ho\end{array}\right.$

Class II. Tertiary Alcohols.

General formula	$C_nH'_{2n-7}Ho$.
Phenylic alcohol. Carbolic acid*	C_6H_5Ho.
Cresylic alcohol	C_6MeH_4Ho.
Phlorol.......................	C_6EtH_4Ho.
Dimethyl-phenylic alcohol	$C_6Me_2H_3Ho$.
Thymylic alcohol...........	$C_6Et_2H_3Ho$?

Class I. *NORMAL ALCOHOLS.*

BENZYLIC ALCOHOL.

$$\left\{\begin{array}{l}C_6H_5\\CH_2Ho\end{array}\right.$$

***Boils at* 204°.**

Preparation.—1. By treating oil of bitter almonds with alcoholic potash :—

$$2\left\{\begin{array}{l}C_6H_5\\COH\end{array}\right. + KHo = \left\{\begin{array}{l}C_6H_5\\CH_2Ho\end{array}\right. + \left\{\begin{array}{l}C_6H_5\\COKo\end{array}\right.$$

Benzoic aldehyde. (Oil of bitter almonds.) — Potassic hydrate. — Benzylic alcohol. — Potassic benzoate.

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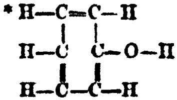
* 

2. Benzylic alcohol may be obtained from toluol by first converting the latter into toluylic chloride by the action of chlorine—

$$\begin{array}{ccccccc} \left\{\begin{matrix} C_6H_5 \\ CH_2H \end{matrix}\right. & + & Cl_2 & = & \left\{\begin{matrix} C_6H_5 \\ CH_2Cl \end{matrix}\right. & + & HCl; \\ \text{Toluol.} & & & & \text{Toluylic chloride.} & & \text{Hydrochloric} \\ \text{(Toluylic hydride.)} & & & & & & \text{acid.} \end{array}$$

and then submitting the toluylic chloride to the action of potassic hydrate:—

$$\begin{array}{ccccccc} \left\{\begin{matrix} C_6H_5 \\ CH_2Cl \end{matrix}\right. & + & KHo & = & \left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right. & + & KCl. \\ \text{Toluylic} & & \text{Potassic} & & \text{Benzylic} & & \text{Potassic} \\ \text{chloride.} & & \text{hydrate.} & & \text{alcohol.} & & \text{chloride.} \end{array}$$

3. By digesting benzylic chloride with freshly precipitated plumbic hydrate:—

$$\begin{array}{ccccccc} 2\left\{\begin{matrix} C_6H_5 \\ CH_2Cl \end{matrix}\right. & + & PbHo_2 & = & PbCl_2 & + & 2\left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right. . \\ \text{Toluylic or} & & \text{Plumbic} & & \text{Plumbic} & & \text{Benzylic alcohol.} \\ \text{Benzylic chloride.} & & \text{hydrate.} & & \text{chloride.} & & \end{array}$$

4. By passing a mixture of hydrogen and the vapour of benzoylic chloride over heated spongy palladium:—

$$\begin{array}{ccccccc} \left\{\begin{matrix} C_6H_5 \\ COCl \end{matrix}\right. & + & 2H_2 & = & \left\{\begin{matrix} C_6H_5 \\ CH_2Ho \end{matrix}\right. & + & HCl. \\ \text{Benzoylic chloride.} & & & & \text{Benzylic alcohol.} & & \end{array}$$

CLASS II. *TERTIARY ALCOHOLS.*

PHENYLIC ALCOHOL, *Carbolic Acid, Phenylic Acid.*

C_6H_5Ho or PhHo.

Molecular weight =94. *Molecular volume* $\square\square$. 1 *litre of phenylic alcohol vapour weighs* 47 *criths. Sp. gr.* 1·065 *at* 18°. *Fuses at* 34°. *Boils at* 188°.

Occurrence.—In coal-tar, and in small quantity in the urine of man, of the cow, and of the horse.

Preparation.—1. By the distillation of salicylic acid with baryta or lime:—

$$\underset{\text{Salicylic acid.}}{\left\{\begin{matrix} C_6H_4Ho \\ COHo \end{matrix}\right.} = \underset{\text{Phenylic alcohol.}}{C_6H_5Ho} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

2. It is also produced in the destructive distillation of numerous organic substances.

3. Phenylic alcohol is formed when the vapour of ethylic alcohol or acetic acid is passed through a red-hot tube. In this manner phenylic compounds may be obtained from their elements; for both acetic acid and alcohol may be built up from carbon, hydrogen, and oxygen.

4. Phenylic alcohol is generated when aniline hydrochlorate is treated with potassic nitrite:—

$$\underset{\text{Aniline hydrochlorate.}}{NPhH_3Cl} + \underset{\text{Potassic nitrite.}}{NOKo} = \underset{\text{Phenylic alcohol.}}{PhHo} + \underset{\text{Potassic chloride.}}{KCl} + \underset{\text{Water.}}{OH_2} + N_2.$$

Reactions.—Treated with chlorine, bromine, or nitric acid, phenylic alcohol produces a series of substitution products, of which the following are examples:—

Dichlorphenylic acid	$C_6H_3Cl_2Ho$.
Trichlorphenylic acid	$C_6H_2Cl_3Ho$.
Perchlorphenylic acid	C_6Cl_5Ho.
Bromphenylic acid	C_6H_4BrHo.
Nitrophenylic acid	$C_6H_4(N^vO_2)Ho$.
Dinitrophenylic acid	$C_6H_3(N^vO_2)_2Ho$.
Trinitrophenylic acid. (*Picric acid.*)	$C_6H_2(N^vO_2)_3Ho$.
Amidodinitrophenylic acid. (*Picramic acid.*)	$C_6H_2(N'''H_2)(N^vO_2)_2Ho$.

CRESYLIC ALCOHOL.

C_6MeH_4Ho.

Boils at 204°.

This alcohol is contained in creosote; it is isomeric with benzylic alcohol.

CHAPTER IX.

DIHYDRIC ALCOHOLS.

Glycol or $C_nH_{2n}Ho_2$ series.

The following is a list of the glycols at present known, with their probable constitutional formulæ:—

				Boiling-points.
Glycol or Ethylic glycol	$C_2H_6O_2$	or	$\left\{\begin{matrix}CH_2Ho\\CH_2Ho\end{matrix}\right.$	197°5.
Propylic glycol...	$C_3H_8O_2$	or	$\left\{\begin{matrix}CMeHHo\\CH_2Ho\end{matrix}\right.$	188°-189°.
Butylic glycol ...	$C_4H_{10}O_2$	or	$\left\{\begin{matrix}CEtHHo\\CH_2Ho\end{matrix}\right.$	183°-184°.
Amylic glycol ...	$C_5H_{12}O_2$	or	$\left\{\begin{matrix}CPrHHo\\CH_2Ho\end{matrix}\right.$	177°.

Methylic glycol has not been obtained.

The existence of normal, secondary, &c. alcohols of this subdivision has not yet been clearly established; but ethylic glycol is probably a normal glycol, whilst propylic, butylic, and amylic glycols are generally considered to be secondary glycols, as shown in the above formulæ.

It will be observed that the boiling-points of the glycols differ from each other in a direction inversely to that previously noticed in the case of the normal monohydric alcohols: the more complex substances boil at a lower temperature than the simpler ones.

GLYCOL. ETHYLIC GLYCOL, *Ethylenic Alcohol.*

$$\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right..$$

Molecular weight = 62. *Molecular volume* □□. 1 *litre of ethylic glycol vapour weighs* 31 *criths. Sp. gr.* 1·125. *Boils at* 197°·5.

Preparation.—Ethylenic dibromide is treated with argentic acetate, and thus converted into ethylenic diacetate:—

$$\underset{\text{Ethylenic dibromide.}}{\left\{\begin{matrix}\mathbf{C}H_2Br\\ \mathbf{C}H_2Br\end{matrix}\right.} + \underset{\text{Argentic acetate.}}{2\mathbf{C}MeOAgo} = \underset{\substack{\text{Ethylenic diacetate.}\\ \text{(Diacetic glycol)}}}{\left\{\begin{matrix}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{matrix}\right.} + \underset{\substack{\text{Argentic}\\ \text{bromide.}}}{2AgBr.}$$

The ethylenic diacetate is now acted upon by potassic hydrate, and yields potassic acetate and glycol:—

$$\underset{\text{Ethylenic diacetate.}}{\left\{\begin{matrix}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo} = \underset{\text{Glycol.}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right.} + \underset{\text{Potassic acetate.}}{2\mathbf{C}MeOKo.}$$

Reactions.—1. Glycol is easily oxidized, the first product of its oxidation being glycollic acid:—

$$\underset{\text{Glycol.}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right.} + O_2 = \underset{\substack{\text{Glycollic}\\ \text{acid}}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water}}{\mathbf{O}H_2.}$$

2. By further oxidation oxalic acid is formed:—

$$\underset{\text{Glycol.}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right.} + O_4 = \underset{\substack{\text{Oxalic}\\ \text{acid}}}{\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.} + \underset{\text{Water.}}{2\mathbf{O}H_2.}$$

3. Potassic oxalate is produced by heating glycol and potassic hydrate together to 250°:—

$$\underset{\text{Glycol.}}{\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo} = \underset{\substack{\text{Potassic}\\ \text{oxalate.}}}{\left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}OKo\end{matrix}\right.} + H_8.$$

4. Treated with potassium or sodium, the hydrogen of the hydroxyl in glycol is replaced in two successive stages:—

$$\left\{\begin{matrix}\mathrm{CH_2Nao}\\ \mathrm{CH_2Ho}\end{matrix}\right. ; \qquad \left\{\begin{matrix}\mathrm{CH_2Nao}\\ \mathrm{CH_2Nao}\end{matrix}\right. .$$

Monosodic glycol. Disodic glycol.

The following list contains some of the principal derivatives of glycol:—

$$\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Ho}\end{matrix}\right. .$$

Glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Hs}\\ \mathrm{CH_2Hs}\end{matrix}\right. .$$

Sulphur glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Cl}\end{matrix}\right. .$$

Chlorhydric glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Br}\end{matrix}\right.$$

Bromhydric glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Eto}\\ \mathrm{CH_2Br}\end{matrix}\right. .$$

Bromethylic glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Eto}\\ \mathrm{CH_2Ho}\end{matrix}\right. .$$

Hydric ethylic glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Eto}\\ \mathrm{CH_2Eto}\end{matrix}\right. .$$

Diethylic glycol.

$$\left\{\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{CH_2}\\ \mathrm{O}\\ \mathrm{CO}\\ \mathrm{CH_3}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{CH_2\text{-}O\text{-}CMeO}\end{matrix}\right. .$$

Glycollic acetobromide.

$$\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2}\\ \mathrm{O}\\ \mathrm{CO}\\ \mathrm{CH_3}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2\text{-}O\text{-}CMeO}\end{matrix}\right. .$$

Monacetic glycol.

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CO}\\ \mathrm{O}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{O}\\ \mathrm{CO}\\ \mathrm{CH_3}\end{matrix}\right. \text{ or } \left\{\begin{matrix}\mathrm{CH_2\text{-}O\text{-}CMeO}\\ \mathrm{CH_2\text{-}O\text{-}CMeO}\end{matrix}\right. .$$

Diacetic glycol.

$$\left\{\begin{array}{l} \mathbf{C}H_3\\ \mathbf{C}O\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}O\\ \mathbf{C}(C_2H_5)H_2 \end{array}\right. \text{ or } \left\{\begin{array}{l} \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}MeO\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}PrO \end{array}\right. .$$

Acetobutyric glycol.

POLYETHYLENIC GLYCOLS,

Polyethylenic Alcohols.

These bodies are produced by heating ethylenic oxide with glycol in sealed tubes, and by other processes. They may be regarded as formed by the addition of ethylenic oxide to glycol.

$$\text{Diethylenic glycol} \ldots \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2Ho \end{array}\right. \text{ or } \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}H_2Ho \end{array}\right. .$$

$$\text{Triethylenic glycol} \ldots \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2Ho \end{array}\right. \text{ or } \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}H_2Ho \end{array}\right. .$$

$$\text{Tetrethylenic glycol} \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ O\\ \mathbf{C}H_2Ho \end{array}\right. \text{ or } \left\{\begin{array}{l} \mathbf{C}H_2Ho\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}_2H_4\\ O\\ \mathbf{C}H_2Ho \end{array}\right. .$$

Pentethylenic and hexethylenic glycols have also been formed.

CHAPTER X.

DIHYDRIC ALCOHOLS.

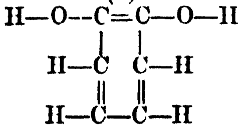
Orcin or $C_nH_{2n-8}Ho_2$ series.

Like the phenyl series, the orcin series of alcohols are the derivatives of benzol. The following alcohols belonging to this series have been described :—

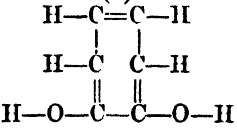
		Melting-point.
Hydroquinone	$C_6H_4Ho_2$ …………	177°·5
Resorcin		99°·0
Pyrocatechin or Oxyphenol		111°·5
Orcin	$C_6MeH_3Ho_2$ ………	86°·0
Homopyrocatechin		——
Betaorcin	$C_6Me_2H_4Ho_2$ ……..	——

Theory indicates the existence of four isomeric bodies of the formula $C_6H_4Ho_2$, the graphic formulæ of which are thus written :—

(1)



(2)



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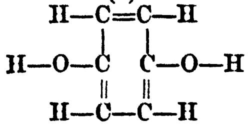
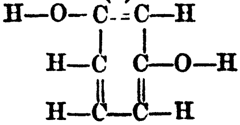


(4)



The isomerism of 1, 3, and 4, and of 2, 3, and 4 is caused (symbolically speaking) by the different distances from each other of the two atoms of carbon with which the two semi-molecules of hydroxyl are combined; in 1 and 2 these carbon atoms are neighbours, in 4 they are separated by one intervening atom of carbon, and in 3 by two intervening atoms of carbon. The isomerism of Nos. 1 and 2 is not equally obvious; indeed it has been overlooked by Kekulé, who considers that three modifications only of the formula $C_6H_4Ho_2$ are possible, unless the six atoms of hydrogen in benzol be not regarded as of equal value. An inspection of the above graphic formulæ shows, however, that a fourth modification is possible, dependent upon the mode in which the two neighbouring atoms of hydroxylic carbon are joined together. In No. 1 these atoms are united by two bonds, in No. 2 by only one bond.

It is at present impossible to assign to each of the three known isomers of $C_6H_4Ho_2$ its own constitutional formula. The same is the case also with the remaining alcohols of this series.

HYDROQUINONE.

$$C_6H_4Ho_2.$$

Preparation.—1. By treating arbutin with emulsin, or by boiling it with dilute sulphuric acid:—

$$\underset{\text{Arbutin.}}{C_{12}H_{16}O_7} + OH_2 = \underset{\text{Hydroquinone.}}{C_6H_4Ho_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

2. By the action of sulphurous acid upon a solution of quinone.

3. By the destructive distillation of quinic acid.

Reactions.—1. Passed in vapour through a red-hot tube, it is decomposed into quinone and hydrogen:—

$$\underset{\text{Hydroquinone.}}{C_6H_4Ho_2} = \underset{\text{Quinone.}}{C_6H_4\left.\begin{matrix}O\\O\end{matrix}\right\}} + H_2.$$

2. By many oxidizing agents it is transformed into quinone:—

$$\underset{\text{Hydroquinone.}}{C_6H_4Ho_2} + O = \underset{\text{Quinone.}}{C_6H_4\left.\begin{matrix}O\\O\end{matrix}\right\}} + OH_2.$$

3. By the action of chlorine or a mixture of potassic chlorate and hydrochloric acid, it is converted into perchloro-quinone (chloranil):—

$$\underset{\text{Hydroquinone.}}{C_6H_4Ho_2} + 3Cl_2 = \underset{\text{Chloranil.}}{C_6Cl_4\left.\begin{matrix}O\\O\end{matrix}\right\}} + 6HCl.$$

ORCIN.

$$C_6MeH_3Ho_2.$$

Melts at 86°. *Boils at about* 290°.

Occurrence.—In certain lichens, such as *Lecanora tartarea*, *Roccella tinctoria*, and *Variolaria orcina*.

Preparation.—By the dry distillation of orsellinic acid, or by boiling this acid with powerful bases:—

$$\underset{\text{Orsellinic acid.}}{C_8H_8O_4} = \underset{\text{Orcin.}}{C_6MeH_3Ho_2} + CO_2.$$

Many other bodies which are obtained from lichens, such as lecanoric acid, erythrin, and picroerythrin, yield orcin under similar treatment; but all these compounds give first orsellinic acid, which then breaks up into orcin and carbonic anhydride; thus:—

$$\underset{\text{Lecanoric acid.}}{C_{16}H_{14}O_7} + OH_2 = \underset{\text{Orsellinic acid.}}{2C_8H_8O_4.}$$

$$\underset{\text{Erythric acid.}}{C_{20}H_{22}O_{10}} + 2OH_2 = \underset{\text{Erythrite.}}{C_4H_{10}O_4} + \underset{\text{Orsellinic acid.}}{2C_8H_8O_4.}$$

$$\underset{\text{Picroerythrin.}}{C_{12}H_{16}O_7} + OH_2 = \underset{\text{Erythrite.}}{C_4H_{10}O_4} + \underset{\text{Orsellinic acid.}}{C_8H_8O_4.}$$

Reactions.—1. With chlorine, bromine, iodine, and nitric acid, orcin gives the following substitution products:—

		Melting-point.
Monobromorcin	$C_6MeH_2BrHo_2$	135°
Tribromorcin	$C_6MeBr_3Ho_2$	103°
Trichlororcin	$C_6MeCl_3Ho_2$	159°
Triiodorcin	$C_6MeI_3Ho_2$	——
Trinitro-orcinic acid ...	$C_6Me(NO_2)_3Ho_2$	162°

2. By treatment with ammonia in the presence of free oxygen it yields orcein, the colouring-matter of *Archil* and *Cudbear*, the reaction being probably the following:—

$$\underset{\text{Orcin.}}{\mathbf{C}_6\mathrm{MeH}_3\mathrm{Ho}_2} + \mathbf{N}\mathrm{H}_3 + \mathrm{O}_3 = \underset{\text{Orcein.}}{\mathbf{C}_6\mathrm{MeH}_3(\mathrm{N^vO_2})\mathrm{Ho}}\,? + 2\mathbf{O}\mathrm{H}_2.$$

3. Heated with an excess of concentrated sulphuric acid to a temperature of from 60° to 80°, orcin yields orcin-disulphuric acid (dihydric orcinic disulphate):—

$$\underset{\text{Sulphuric acid.}}{2\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2} + \underset{\text{Orcin.}}{\mathbf{C}_6\mathrm{MeH}_3\mathrm{Ho}_2} = \underset{\text{Dihydric orcinic disulphate.}}{\begin{matrix}\mathbf{S}\mathrm{O}_2\mathrm{Ho}\\ \mathbf{S}\mathrm{O}_2\mathrm{Ho}\end{matrix}(\mathbf{C}_6\mathrm{MeH}_2\mathrm{O}_2)''} + 2\mathbf{O}\mathrm{H}_2.$$

CHAPTER XI.

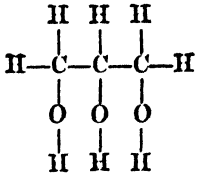
TRIHYDRIC ALCOHOLS.

Glycerin or $C_nH_{2n-1}Ho_3$ series.

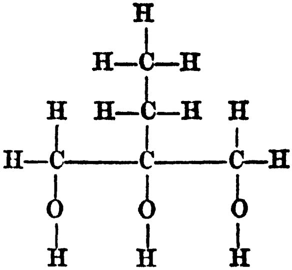
These alcohols contain three semimolecules of hydroxyl united with three different atoms of carbon; consequently the lowest term of the series contains three atoms of carbon.

Only two of these alcohols have been hitherto obtained:—

Glycerin .... $\left\{\begin{matrix}\mathbf{C}\mathrm{H}_2\mathrm{Ho}\\ \mathbf{C}\mathrm{HHo}\\ \mathbf{C}\mathrm{H}_2\mathrm{Ho}\end{matrix}\right.$.



Amylglycerin ... $\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}EtHo\,?\\ \mathbf{C}H_2Ho\end{array}\right.$



The constitution of amylglycerin is not at present established. Its formula may possibly be

$$\left\{\begin{array}{l}\mathbf{C}EtHHo\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right. .$$

The action of oxidizing agents on amylglycerin will probably throw light upon its internal structure.

GLYCERIN.

$$\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right. .$$

Sp. gr. of liquid at 15°·4 *is* 1·26. *Crystallizes at low temperatures, and remains solid afterwards at ordinary temperatures. Boils in vacuo at* 179°·5.

Sources.—Most animal and vegetable fats consist of mixtures of the glycerin ethereal salts of the fatty, and of the oleic, series of acids. Glycerin is liberated from these by water at high temperatures, or by bases giving salts insoluble in water:—

$$\underset{\text{Stearin.}}{\left\{\begin{array}{l}\mathbf{C}H_2\text{-}O\text{-}\mathbf{C}(C_{17}H_{35})O\\ \mathbf{C}H\text{-}O\text{-}\mathbf{C}(C_{17}H_{35})O\\ \mathbf{C}H_2\text{-}O\text{-}\mathbf{C}(C_{17}H_{35})O\end{array}\right.} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} + 3\underset{\text{Stearic acid.}}{\left\{\begin{array}{l}C_{17}H_{35}\\ \mathbf{C}OHo\end{array}\right.} .$$

Relation of Glycerin to Isopropylic Alcohol.

By the action of hydriodic acid, glycerin is converted into isopropylic iodide:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} + \underset{\text{Hydriodic acid.}}{5HI} = \underset{\text{Isopropylic iodide.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}HI\\ \mathbf{C}H_3\end{array}\right.} + 2I_2 + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Relation of Glycerin to Allylic Alcohol.

When diphosphorous tetriodide is brought into contact with glycerin, an energetic reaction ensues, allylic iodide being formed:—

$$\underset{\text{Diphosphorous tetriodide.}}{\mathbf{P}''_2I_4} + 2\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} = 2''\underset{\text{Allylic iodide.}}{\left\{\begin{array}{l}\mathbf{C}H_2\\ \mathbf{C}H\\ \mathbf{C}H_2I\end{array}\right.} + \underset{\text{Phosphorous acid.}}{2\mathbf{PO}HHo_2} + I_2.$$

Relations of Glycerin to Propylic Glycol.

The several semimolecules of hydroxyl in glycerin are capable of being replaced by chlorine, bromine, &c.; thus, by the action of hydrochloric acid on glycerin, one semimolecule of hydroxyl is displaced by chlorine, monochlorhydrin being formed:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Monochlorhydrin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Monochlorhydrin is identical with monochlorinated propylic glycol:—

$$\underset{\text{Monochlorhydrin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} = \underset{\text{Monochlorinated propylic glycol.}}{\left\{\begin{array}{l}\mathbf{C}(\mathbf{C}H_2Cl)HHo\\ \mathbf{C}H_2Ho\end{array}\right.}.$$

By the action of sodium amalgam and water, monochlorinated propylic glycol is readily converted into propylic glycol:—

$$\underset{\text{Monochlorinated propylic glycol.}}{\left\{\begin{matrix}C(CH_2Cl)HHo\\ CH_2Ho\end{matrix}\right.} + H_2 = \underset{\text{Propylic glycol.}}{\left\{\begin{matrix}C(CH_3)HHo\\ CH_2Ho\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

Relations of Glycerin to the Trihydric Acids—Glyceric Acid and Tartronic Acid.

By the slow action of nitric acid, glycerin is converted into glyceric acid:—

$$\underset{\text{Glycerin.}}{\left\{\begin{matrix}CH_2Ho\\ CHHo\\ CH_2Ho\end{matrix}\right.} + O_2 = \underset{\text{Glyceric acid.}}{\left\{\begin{matrix}CH_2Ho\\ CHHo\\ COHo\end{matrix}\right.} + \underset{\text{Water.}}{OH_2.}$$

A second semimolecule of oxatyl has not been produced in glycerin, so as to convert the latter into a dibasic acid; but there can be little doubt that tartronic acid, which is formed by the spontaneous decomposition of nitrotartaric acid, is the acid in question, and that it has the following constitution:—

$$\underset{\text{Tartronic acid.}}{\left\{\begin{matrix}COHo\\ CHHo.\\ COHo\end{matrix}\right.}$$

Relations of Glycerin to Acrylic Acid.

By the action of substances having an affinity for water, such as phosphoric anhydride or sulphuric acid, glycerin is converted into acrolein:—

$$\underset{\text{Glycerin.}}{\left\{\begin{matrix}CH_2Ho\\ CHHo\\ CH_2Ho\end{matrix}\right.} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Acrolein.}}{\left\{\begin{matrix}CMe''H\\ COH\end{matrix}\right.}.$$

By the absorption of oxygen, acrolein is transformed into acrylic acid:—

$$\underset{\text{Acrolein.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COH}\end{array}\right.} + \mathrm{O} = \underset{\text{Acrylic acid.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right.}.$$

Both these reactions are accomplished simultaneously when glycerin is added to fused potassic hydrate:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHHo}\\ \mathrm{CH_2Ho}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} = \underset{\text{Potassic acrylate.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COKo}\end{array}\right.} + \mathrm{H_2} + \underset{\text{Water.}}{2\mathrm{OH_2}}.$$

CHAPTER XII.

TRIHYDRIC ALCOHOLS.

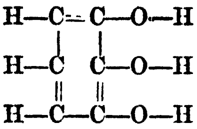
Pyrogallic or $C_nH_{2n-9}Ho_3$ series.

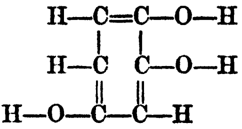
Like the phenyl and orcin series, these alcohols are the direct derivatives of benzol.

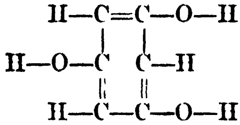
The following bodies are believed to belong to this series, whilst several other compounds not yet sufficiently known will probably soon be added to it:—

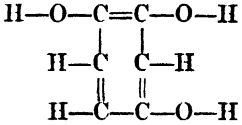
		Melting-point.
Pyrogallin	$C_6H_3Ho_3$	115°.
Phloroglucin		220°.
Phenomalic acid ? ...		——

Theory points to four isomeric modifications of the formula $C_6H_3Ho_3$, viz.:—









It is at present impossible to assign any of these formulæ to the above enumerated three members of this series of alcohols.

PYROGALLIN, *Pyrogallic Acid.*

$C_6H_3Ho_3$.

Melts at 115°. *Sublimes with partial decomposition at* 210°.

Preparation.—1. By heating gallic acid to 210°–220° in a stream of carbonic anhydride:—

Gallic acid. Pyrogallin.

2. By heating gallic acid with twice or thrice its weight of water to 200°–210° for half an hour in a Papin's digester. The reaction is the same as in No. 1.

Reactions.—1. Does not neutralize alkalies or form true salts.

2. Passed over heated zinc, it is transformed into benzol:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} + 3Zn = \underset{\text{Benzol.}}{C_6H_6} + 3ZnO.$$

3. Bromine converts pyrogallin into tribromopyrogallin:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} + 3Br_2 = \underset{\text{Tribromopyrogallin.}}{C_6Br_3Ho_3} + 3HBr.$$

4. Heated to 250°, it yields water and metagallic acid:—

$$\underset{\text{Pyrogallin.}}{C_6H_3Ho_3} = \underset{\text{Metagallic acid.}}{C_6H_3OHo} + OH_2.$$

5. Ammonia in the presence of air forms with it pyrogallein, to which the formula $C_{18}H_{20}N_6O_{10}$ has been assigned.

6. Concentrated boiling solution of caustic potash decomposes it into acetic, oxalic, and carbonic acids.

7. An alkaline solution of pyrogallin rapidly absorbs free oxygen, forming a dark-coloured body, together with acetic and carbonic acids and a small quantity of carbonic oxide.

OTHER POLYHYDRIC ALCOHOLS.

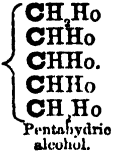
Erythrite (*Erythroglucin*, *Erythromannite*, *Phycite*, *Pseudorcin*) is a tetrahydric alcohol; and the acid corresponding to it is tartaric acid. Citric acid may also be considered as derived from an unknown alcohol of this series. A glance at the formulæ of these alcohols and acids will show their relations:—

$$\underset{\text{Erythrite.}}{\left\{\begin{array}{l}CH_2Ho\\ CHHo\\ CHHo\\ CH_2Ho\end{array}\right.}\cdot \quad \underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}COHo\\ CHHo\\ CHHo\\ COHo\end{array}\right.}\cdot \quad \Bigg| \quad \underset{\text{Tetrahydric alcohol (unknown).}}{\left\{\begin{array}{l}CHHo(CH_2Ho)\\ CH(CH_2Ho)\\ CH_2(CH_2Ho)\end{array}\right.}. \quad \underset{\text{Citric acid.}}{\left\{\begin{array}{l}CHHo(COHo)\\ CH(COHo)\\ CH_2(COHo)\end{array}\right.}.$$

When reduced by hydriodic acid, erythrite yields butylic iodide:—

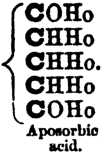
$$\underset{\text{Erythrite.}}{\left\{\begin{array}{l}CH_2Ho\\ CHHo\\ CHHo\\ CH_2Ho\end{array}\right.} + \underset{\text{Hydriodic acid.}}{7HI} = \underset{\text{Water.}}{4OH_2} + \underset{\text{Butylic iodide.}}{\left\{\begin{array}{l}CH_3\\ CH_2\\ CH_2\\ CH_2I\end{array}\right.} + 3I_2.$$

Pinite and *Quercite* are believed to be pentahydric alcohols; and aposorbic acid is probably a derivative of one of them:—



$$\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CHHo. \\ CHHo \\ CH_2Ho \end{array}\right.$$

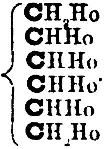
Pentahydric alcohol.



$$\left\{\begin{array}{l} COHo \\ CHHo \\ CHHo. \\ CHHo \\ COHo \end{array}\right.$$

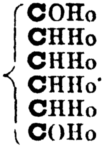
Aposorbic acid.

Mannite is a hexahydric alcohol. There are three acids corresponding to this alcohol: these are saccharic and mucic acids, which are isomeric, and mannitic acid:—



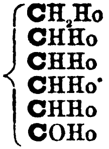
$$\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CHHo \\ CHHo\cdot \\ CHHo \\ CH_2Ho \end{array}\right.$$

Mannite.



$$\left\{\begin{array}{l} COHo \\ CHHo \\ CHHo \\ CHHo\cdot \\ CHHo \\ COHo \end{array}\right.$$

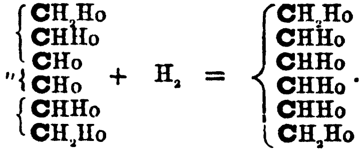
Saccharic or mucic acid.



$$\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CHHo \\ CHHo\cdot \\ CHHo \\ COHo \end{array}\right.$$

Mannitic acid.

Mannite is closely related to *glucose*, the latter containing two atoms of hydrogen less than the former. Glucose can, in fact, be converted into mannite by the action of nascent hydrogen:—



$$\left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CHo \\ CHo \\ CHHo \\ CH_2Ho \end{array}\right. + H_2 = \left\{\begin{array}{l} CH_2Ho \\ CHHo \\ CHHo \\ CHHo\cdot \\ CHHo \\ CH_2Ho \end{array}\right.$$

Glucose. Mannite.

Alcohols of high hydricity possess a sweet taste, in fact with increase of hydricity the alcohols gradually pass into saccharine substances or sugars.

CHAPTER XIII.

THE ETHERS.

These compounds are the oxides of the positive radicals.

Each series of alcohols produces a series of ethers; we have thus ethers of the monohydric, dihydric, and trihydric alcohols, of which the following are the general formulæ :—

	Methyl series	Vinyl series.	Phenyl series.
Ethers of the monohydric alcohols	$\left\{\begin{array}{l} C_nH_{2n+1} \\ O \\ C_nH_{2n+1} \end{array}\right.$	$\left\{\begin{array}{l} C_nH_{2n-1} \\ O \\ C_nH_{2n-1} \end{array}\right.$	$\left\{\begin{array}{l} C_nH_{2n-7} \\ O \\ C_nH_{2n-7} \end{array}\right.$.

Ethers of the dihydric alcohols .. $C_nH_{2n}O$.

Ethers of the trihydric alcohols $\left\{\begin{array}{l} C_nH_{2n}\text{-}O\text{-}H_{2n}C_n \\ C_nH_{2n-1}\text{-}O\text{-}H_{2n-1}C_n \\ C_nH_{2n}\text{-}O\text{-}H_{2n}C_n \end{array}\right\}$.

ETHERS OF THE MONOHYDRIC ALCOHOLS.

These bodies are derived from the alcohols by the substitution of the hydroxylic hydrogen contained in the latter by a positive monad radical.

METHYL SERIES.

The following list contains some of the ethers of this series :—

						Boiling-points.
Methylic ether			$\left\{\begin{array}{l} CH_3 \\ O \\ CH_3 \end{array}\right.$	or	OMe_2	$-21°$.
Methylicethylicether	$\left\{\begin{array}{l} CH_3 \\ O \\ C_2H_5 \end{array}\right.$	or	$\left\{\begin{array}{l} CH_3 \\ O \\ CMeH_2 \end{array}\right.$	or	$OMeEt$	$+11°$.
Ethylic ether	$\left\{\begin{array}{l} C_2H_5 \\ O \\ C_2H_5 \end{array}\right.$	or	$\left\{\begin{array}{l} CMeH_2 \\ O \\ CMeH_2 \end{array}\right.$	or	OEt_2	35°·6.
Methylicamylicether	$\left\{\begin{array}{l} CH_3 \\ O \\ C_5H_{11} \end{array}\right.$	or	$\left\{\begin{array}{l} CH_3 \\ O \\ CBuH_2 \end{array}\right.$	or	$OMeAy$	92°.

						Boiling points.
Ethylic butylic ether.	$\left\{\begin{matrix}C_2H_5\\ O\\ C_4H_9\end{matrix}\right.$	or	$\left\{\begin{matrix}CMeH_2\\ O\\ CPrH_2\end{matrix}\right.$	or	$OEtBu$	80°?.
Ethylic amylic ether.	$\left\{\begin{matrix}C_2H_5\\ O\\ C_5H_{11}\end{matrix}\right.$	or	$\left\{\begin{matrix}CMeH_2\\ O\\ CBuH_2\end{matrix}\right.$	or	$OEtAy$	112°.
Butylic ether	$\left\{\begin{matrix}C_4H_9\\ O\\ C_4H_9\end{matrix}\right.$	or	$\left\{\begin{matrix}CPrH_2\\ O\\ CPrH_2\end{matrix}\right.$	or	OBu_2	104°.
Amylic ether	$\left\{\begin{matrix}C_5H_{11}\\ O\\ C_5H_{11}\end{matrix}\right.$	or	$\left\{\begin{matrix}CBuH_2\\ O\\ CBuH_2\end{matrix}\right.$	or	OAy_2	176°.

Formation.—1. By the action of sulphuric acid upon the $C_nH_{2n+1}Ho$ alcohols. The process may be divided into the two following stages:—

$$\underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} + \underset{\text{Sulphuric acid}}{SO_2Ho_2} = \underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Alcohol}}{C_nH_{2n+1}Ho} = \underset{\text{Ether}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

2. By converting the $C_nH_{2n+1}Ho$ alcohols into sodium or potassium compounds, and then acting upon the latter with the iodides of the monad positive radicals:—

$$\underset{\text{Alcohol}}{2C_nH_{2n+1}Ho} + Na_2 = \underset{\text{Sodic alcohol.}}{2C_nH_{2n+1}Nao} + H_2.$$

$$\underset{\text{Sodic alcohol.}}{C_nH_{2n+1}Nao} + \underset{\text{Iodide}}{C_nH_{2n+1}I} = \underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sodic iodide.}}{NaI}.$$

Reaction.—The ethers can be reconverted into the corresponding alcohols by treating them with sulphuric acid, and then distilling, with water, the sulpho-acid so produced:—

$$\underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{2SO_2Ho_2} = \underset{\text{Sulpho-acid.}}{2SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Sulpho-acid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Alcohol.}}{C_nH_{2n+1}Ho}.$$

METHYLIC ETHER, *Methylic Oxide.*

$$\left\{\begin{array}{l}\mathbf{C}H_3\\ O\\ \mathbf{C}H_3\end{array}\right. \text{ or } \mathbf{O}Me_2.$$

Molecular weight =46. *Molecular volume* □□. 1 *litre of methylic ether vapour weighs* 23 *criths. Boils at* −21°.

Preparation.—By heating methylic alcohol with sulphuric acid or boric anhydride:—

$$\underset{\text{Methylic alcohol}}{\mathbf{C}H_3Ho} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Sulphomethylic acid}}{\mathbf{S}O_2Ho(\mathbf{C}H_3O)} + \underset{\text{Water}}{\mathbf{O}H_2};$$

$$\underset{\text{Sulphomethylic acid.}}{\mathbf{S}O_2Ho(\mathbf{C}H_3O)} + \underset{\text{Methylic alcohol}}{\mathbf{C}H_3Ho} = \underset{\text{Methylic ether}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ O\\ \mathbf{C}H_3\end{array}\right.} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2}.$$

Reaction.—Methylic ether is acted upon by chlorine under the influence of light, the hydrogen being displaced atom for atom by chlorine. The following compounds are formed:—

$$\underset{\text{Dichlorinated methylic ether}}{\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ O\\ \mathbf{C}H_2Cl\end{array}\right.};\quad \underset{\text{Tetrachlorinated methylic ether}}{\left\{\begin{array}{l}\mathbf{C}HCl_2\\ O\\ \mathbf{C}HCl_2\end{array}\right.};\quad \underset{\text{Perchlorinated methylic ether.}}{\left\{\begin{array}{l}\mathbf{C}Cl_3\\ O\\ \mathbf{C}Cl_3\end{array}\right.}.$$

ETHYLIC ETHER, *Ethylic Oxide, Ether, Sulphuric Ether.*

$$\left\{\begin{array}{l}\mathbf{C}MeH_2\\ O\\ \mathbf{C}MeH_2\end{array}\right. \text{ or } \mathbf{O}Et_2.$$

Molecular weight =74. *Molecular volume* □□.* 1 *litre of ether vapour weighs* 37 *criths. Sp. gr.* =0·723. *Fuses at* −31°. *Boils at* 35°·6.

Preparation.—A mixture of equal volumes of sulphuric acid and alcohol is heated to a temperature of from 140° to 145°, and a constant stream of alcohol is allowed to flow into the mixture. Ether and water distil over together. Two reactions take place successively: in the first, the alcohol is converted into sulphovinic acid; and in the second the sulphovinic acid is converted by a further quantity of alcohol into sulphuric acid and ether:—

$$\underset{\text{Alcohol.}}{EtHo} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Sulphovinic acid.}}{SO_2EtoHo} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Sulphovinic acid.}}{SO_2EtoHo} + \underset{\text{Alcohol.}}{EtHo} = \underset{\text{Ether.}}{OEt_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

In this manner the same quantity of sulphuric acid can convert an unlimited quantity of alcohol into ether.

The formation of ether is not due to the simple removal of water from two molecules of alcohol by sulphuric acid. This is proved, first, by the sulphuric acid not becoming more dilute, and, secondly, by the fact that, if sulphamylic acid be acted upon by ethylic alcohol, the mixed ethylic amylic ether is formed:—

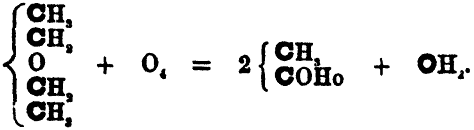
$$\underset{\text{Sulphamylic acid.}}{SO_2AyoHo} + \underset{\text{Ethylic alcohol.}}{EtHo} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Ethylic amylic ether.}}{OAyEt}.$$

Reactions.—1. Ethylic ether, when mixed with an equal volume of sulphuric acid, produces sulphovinic acid:—

$$\underset{\text{Ethylic ether.}}{OEt_2} + \underset{\text{Sulphuric acid.}}{2SO_2Ho_2} = \underset{\text{Sulphovinic acid.}}{2SO_2EtoHo} + \underset{\text{Water.}}{OH_2}.$$

2. Hot nitric acid converts ethylic ether into carbonic, acetic, and oxalic acids.

3. Exposed to the air, it gradually absorbs oxygen and is transformed into acetic acid:—



$$\underset{\text{Ethylic ether.}}{\left\{\begin{matrix} CH_3 \\ CH_2 \\ O \\ CH_2 \\ CH_3 \end{matrix}\right.} + O_4 = 2\underset{\text{Acetic acid.}}{\left\{\begin{matrix} CH_3 \\ COHo \end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

ETHYLIC SULPHIDE, *Sulphur Ether.*

$$\left\{\begin{matrix}\mathbf{C}\mathrm{MeH}_2\\ \mathbf{S}\\ \mathbf{C}\mathrm{MeH}_2\end{matrix}\right. \text{ or } \mathbf{S}\mathrm{Et}_2.$$

Molecular weight =90. *Molecular volume* ☐☐. 1 *litre of ethylic sulphide vapour weighs* 45 *criths. Boils at* 73°.

Preparation.—By adding ethylic chloride to potassic sulphide, and distilling:—

$$\underset{\text{Ethylic chloride.}}{2\mathbf{C}\mathrm{MeH}_2\mathrm{Cl}} + \underset{\substack{\text{Potassic}\\ \text{sulphide.}}}{\mathbf{S}\mathrm{K}_2} = \underset{\text{Ethylic sulphide.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{MeH}_2\\ \mathbf{S}\\ \mathbf{C}\mathrm{MeH}_2\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\ \text{chloride.}}}{2\mathrm{KCl}}.$$

Reactions.—1. Ethylic sulphide combines directly with ethylic iodide, forming

Sulphurous triethylo-iodide .... $\mathbf{S}\mathrm{Et}_3\mathrm{I}$.

By the action of argentic oxide on this iodide, the corresponding hydrate may be formed:—

$$\underset{\substack{\text{Sulphurous}\\ \text{triethylo-}\\ \text{iodide.}}}{\mathbf{S}\mathrm{Et}_3\mathrm{I}} + \underset{\substack{\text{Argentic}\\ \text{hydrate.}}}{\mathrm{AgHo}} = \underset{\substack{\text{Sulphurous}\\ \text{triethylo-}\\ \text{hydrate.}}}{\mathbf{S}\mathrm{Et}_3\mathrm{Ho}} + \underset{\substack{\text{Argentic}\\ \text{iodide.}}}{\mathrm{AgI}}.$$

2. By cold nitric acid it is converted into sulphurous diethoxide ($\mathbf{S}\mathrm{OEt}_2$), which by more powerful oxidizing agents is transformed into diethylsulphon (sulphuric diethoxide), $\mathbf{S}\mathrm{O}_2\mathrm{Et}_2$, which melts at 70° and boils at 248°.

ETHERS OF THE VINYL AND PHENYL SERIES.

Of the ethers of the vinyl series, allylic ether, $\left\{\begin{matrix}\mathbf{C}_3\mathrm{H}_5\\ \mathrm{O}\\ \mathbf{C}_3\mathrm{H}_5\end{matrix}\right.$, alone is known. It boils at 82°.

In the phenyl series, phenylic ether, $\left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathrm{O}\\ \mathbf{C}_6\mathrm{H}_5\end{matrix}\right.$, and benzylic ether, $\left\{\begin{matrix}\mathbf{C}_7\mathrm{H}_7\\ \mathrm{O}\\ \mathbf{C}_7\mathrm{H}_7\end{matrix}\right.$, have been obtained.

By digesting benzylic chloride with potassic phenylate, a mixed ether, phenyl-benzyl ether, is formed:—

$$\underset{\text{Benzylic chloride.}}{\left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CH_2Cl}\end{matrix}\right.} + \underset{\text{Potassic phenylate.}}{\mathrm{C_6H_5Ko}} = \underset{\text{Potassic chloride.}}{\mathrm{KCl}} + \underset{\text{Phenyl-benzyl ether.}}{\left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CH_2}\\ \mathrm{O}\\ \mathrm{C_6H_5}\end{matrix}\right.}.$$

ETHERS OF THE DIHYDRIC ALCOHOLS.

Of these the three following are known, but the first only has been carefully studied:—

		Boiling-points.
Ethylenic oxide,	C_2H_4O	13°·5.
Propylenic oxide,	C_3H_6O	35°·0.
Amylenic oxide,	$C_5H_{10}O$	95°·0.

ETHYLENIC OXIDE, *Ethylenic Ether.*

$$\mathrm{C_2H_4O} = \left\{\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\right.\mathrm{O}.$$

Molecular weight =44. *Molecular volume* □□. 1 *litre of ethylenic oxide vapour weighs* 22 *criths. Boils at* 13°·5.

Preparation.—Ethylenic oxide is obtained from glycol by converting the latter, first into ethylenic chlorhydrate, or chlorhydric glycol, by the action of hydrochloric acid, and subsequently treating the compound thus formed with potassic hydrate:—

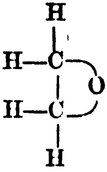
$$\underset{\text{Glycol.}}{\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Ho}\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Ethylenic chlorhydrate.}}{\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Cl}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}:$$

$$\underset{\text{Ethylenic chlorhydrate.}}{\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CH_2Cl}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} = \underset{\text{Ethylenic oxide.}}{\left\{\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}\right.\mathrm{O}} + \underset{\text{Water.}}{\mathrm{OH_2}} + \underset{\text{Potassic chloride.}}{\mathrm{KCl}}.$$

Isomers.—Ethylenic oxide is isomeric with vinylic alcohol and acetic aldehyde. The nature of this isomerism is seen in the following formulæ:—

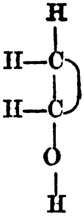
$\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH_2}\end{array}\right.O.$

Ethylenic oxide.



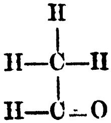
$\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH}Ho\end{array}\right.\cdot$

Vinylic alcohol.



$\left\{\begin{array}{l}\mathbf{CH_3}\\ \mathbf{CO}H\end{array}\right.\cdot$

Acetic aldehyde.



Reactions.—1. Ethylenic oxide unites with nascent hydrogen, forming alcohol:—

$$\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH_2}\end{array}\right.O + H_2 = \left\{\begin{array}{l}\mathbf{CH_3}\\ \mathbf{CH_2}Ho\end{array}\right.\cdot$$

Ethylenic oxide. Alcohol.

2. It also unites with oxygen, forming glycollic acid:—

$$\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH_2}\end{array}\right.O + O_2 = \left\{\begin{array}{l}\mathbf{CH_2}Ho\\ \mathbf{CO}Ho\end{array}\right.\cdot$$

Ethylenic oxide. Glycollic acid.

3. It is a basic substance, and unites directly with acids:—

$$\left\{\begin{array}{l}\mathbf{CH_2}\\ \mathbf{CH_2}\end{array}\right.O + HCl = \left\{\begin{array}{l}\mathbf{CH_2}Cl\\ \mathbf{CH_2}Ho\end{array}\right.\cdot$$

Ethylenic oxide. Hydrochloric acid. Ethylenic chlorhydrate or chlorhydric glycol.

4. Ethylenic oxide precipitates as hydrates many metals from

solutions of their salts, such as the ferric, aluminic, cupric, and magnesic hydrates:—

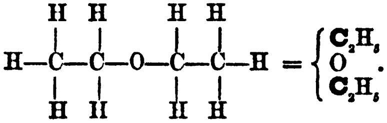
$$2\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O + MgCl_2 + 2OH_2 = 2\left\{\begin{matrix}CH_2Cl\\CH_2Ho\end{matrix}\right. + MgHo_2.$$
$$\begin{matrix}\text{Ethylenic oxide.} & \text{Magnesic chloride.} & \text{Water.} & \text{Ethylenic chlorhydrate.} & \text{Magnesic hydrate.}\end{matrix}$$

5. It also combines directly with water, reproducing glycol:—

$$\left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O + OH_2 = \left\{\begin{matrix}CH_2Ho\\CH_2Ho\end{matrix}\right..$$
$$\begin{matrix}\text{Ethylenic oxide.} & \text{Water.} & \text{Glycol.}\end{matrix}$$

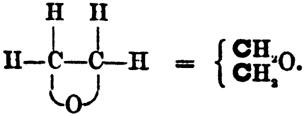
These reactions exhibit a wide difference between the behaviour of ethylenic ether and that of ethylic ether. This difference arises from the fact, that in ethylic ether the ethyl semimolecules are held together by the oxygen only, whereas in ethylenic ether the linking of the two groups of CH_2 does not depend on the oxygen atom alone, as will be seen from the following formulæ:—

Ethylic ether ....



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H = \left\{\begin{matrix}C_2H_5\\O\\C_2H_5\end{matrix}\right..$$

Ethylenic ether ......



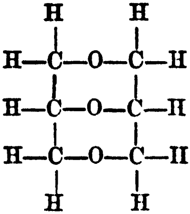
$$= \left\{\begin{matrix}CH_2\\CH_2\end{matrix}\right.O.$$

On account of this peculiarity of constitution, ethylenic oxide can combine directly with many substances without the disruption of its molecule,—a property which obviously cannot be possessed by ethylic ether.

ETHERS OF THE TRIHYDRIC ALCOHOLS.

Of these only one is known, viz.:—

GLYCYLIC ETHER, *Glycylic Oxide.*



$$= \left\{\begin{array}{l} \mathrm{CH_2\text{-}O\text{-}H_2C} \\ \mathrm{CH\ \text{-}O\text{-}H\ C} \\ \mathrm{CH_2\text{-}O\text{-}H_2C} \end{array}\right\}.$$

Preparation.—By the action of potassic hydrate on so-called iodhydrin:—

$$\left\{\begin{array}{l} \left.\begin{array}{l}\mathrm{CH_2}\\ \mathrm{CH}\end{array}\right.\mathrm{O} \\ \mathrm{CH_2} \\ \mathrm{O} \\ \mathrm{CH_2} \\ \mathrm{CHI} \\ \mathrm{CH_2Ho} \end{array}\right. + \mathrm{KHo} = \mathrm{KI} + \mathrm{OH_2} + \left\{\begin{array}{l} \mathrm{CH_2\text{-}O\text{-}H_2C} \\ \mathrm{CH\ \text{-}O\text{-}H\ C} \\ \mathrm{CH_2\text{-}O\text{-}H_2C} \end{array}\right\}.$$

Iodhydrin. Potassic hydrate. Potassic iodide. Water. Glycylic ether.

CHAPTER XIV.

THE HALOID ETHERS.

EACH series of positive radicals forms its own series of haloid ethers.

These ethers are produced by the substitution of hydroxyl in the alcohols by chlorine, bromine, iodine, fluorine, or cyanogen.

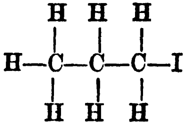
Haloid Ethers of the Monad Positive Radicals.

As these radicals can only unite with one semimolecule of hydroxyl, they can only form one haloid ether. Each series of radicals therefore forms one series of haloid ethers :—

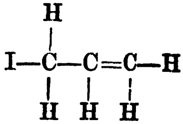
I. Haloid ethers of the form $C_nH_{2n+1}Cl$.
II. „ „ „ „ $C_nH_{2n-1}Cl$.
III. „ „ „ „ $C_nH_{2n-7}Cl$.

The following will serve as examples of the three series :—

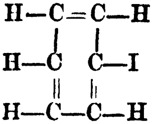
Propylic iodide... C_3H_7I or $C(C_2H_5)H_2I$.



Allylic iodide ... C_3H_5I or $C(C_2H_3)H_2I$.



Phenylic iodide C_6H_5I



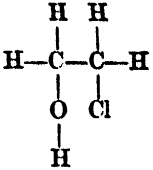
Haloid Ethers of the Dyad Positive Radicals.

As the dihydric alcohols contain two semimolecules of hydroxyl, it follows that there are two classes of haloid ethers derivable from them. The first is formed by the substitution of one of the semimolecules of hydroxyl by chlorine, bromine, &c., and the second by the like displacement of both semimolecules of hydroxyl :—

I. Haloid ethers of the form $C_nH_{2n}HoCl$.
II. „ „ „ „ $C_nH_{2n}Cl_2$.

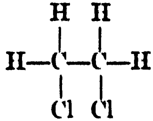
The following examples will suffice to illustrate the constitution of both these classes of haloid ethers :—

Chlorhydric glycol or ethylenic chlorhydrate......... C_2H_4HoCl or $\left\{\begin{array}{l}CH_2Ho\\CH_2Cl\end{array}\right.$



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & O & & Cl & & \\ & & | & & & & \\ & & H & & & & \end{array}$$

Ethylenic dichloride .... $C_2H_4Cl_2$ or $\left\{\begin{array}{l}CH_2Cl\\CH_2Cl\end{array}\right.$



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$

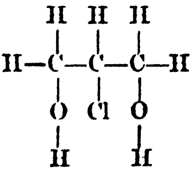
Haloid Ethers of the Triad Positive Radicals.

Three classes of haloid ethers are derived from the trihydric alcohols by the successive substitution of the three semimolecules of hydroxyl contained in these alcohols by chlorine, bromine, &c. A fourth class also exists, which stands intermediate between the ethers and the haloid ethers, and which is formed by the substitution of one of the semimolecules of hydroxyl in the alcohol by a monad negative radical, such as chlorine, bromine, or cyanogen, and the remaining two semimolecules of hydroxyl by a dyad oxygen:—

I. Haloid ethers of the form $C_nH_{2n-1}Ho_2Cl$.
II. " " " $C_nH_{2n-1}HoCl_2$.
III. " " " $C_nH_{2n-1}Cl_3$.
IV. " " " $C_nH_{2n-1}OCl$.

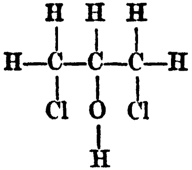
The following are examples of each of these classes:—

Chlorhydrin. $\left\{\begin{array}{l}CH_2Ho\\CHCl\\CH_2Ho\end{array}\right.$

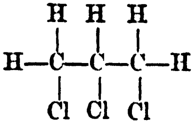


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & O & & Cl & & O & & \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

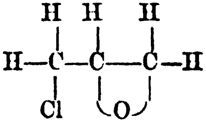
$$\text{Dichlorhydrin} \ldots \left\{\begin{array}{l} CH_2Cl \\ CHHo. \\ CH_2Cl \end{array}\right.$$



$$\text{Trichlorhydrin} \ldots \left\{\begin{array}{l} CH_2Cl \\ CHCl\,. \\ CH_2Cl \end{array}\right.$$



$$\begin{array}{l}\text{Hydrochloric} \\ \quad\text{glycide or epi-} \\ \quad\text{chlorhydrin} \ldots\end{array} \left\{\begin{array}{l} CH_2Cl \\ \left.\begin{array}{l} CH \\ CH_2 \end{array}\right\rangle O\,. \end{array}\right.$$



HALOID ETHERS OF THE MONAD POSITIVE RADICALS.

Preparation.—These ethers are produced by the following general reactions :—

1. By the action of the hydracids upon the alcohols :—

$$\underset{\text{Alcohol.}}{C_nH_{2n+1}Ho} + \underset{\substack{\text{Hydrochloric} \\ \text{acid.}}}{HCl} = \underset{\text{Haloid ether.}}{C_nH_{2n+1}Cl} + \underset{\text{Water.}}{OH_2}.$$

2. By the action of phosphorous chloride on the alcohols:—

$$\underset{\text{Alcohol.}}{3C_nH_{2n+1}Ho} + \underset{\substack{\text{Phosphorous} \\ \text{chloride.}}}{PCl_3} = \underset{\text{Haloid ether.}}{3C_nH_{2n+1}Cl} + \underset{\substack{\text{Phosphorous} \\ \text{acid.}}}{POHHo_2}.$$

3. By the action of chlorine on the hydrides of the radicals :—

$$\underset{\text{Hydride.}}{C_nH_{2n+1}H} + Cl_2 = \underset{\text{Haloid ether.}}{C_nH_{2n+1}Cl} + \underset{\substack{\text{Hydrochloric} \\ \text{acid.}}}{HCl}.$$

It is obvious that in these reactions bromine and iodine may be used instead of chlorine.

These reactions apply equally to the C_nH_{2n-1} and C_nH_{2n-7} series.

For the preparation of the nitriles, which are isomeric with the cyanides of the radicals, two special reactions (Nos. 1 and 2) are employed.

1. The distillation in the dry state of a mixture of the potassic sulphate of the radical with potassic cyanide:—

$$\mathbf{S}O_2Ko(C_nH_{2n+1}O) + KCy = \mathbf{S}O_2Ko_2 + C_nH_{2n+1}Cy.$$

Potassic sulphate of the radical. Potassic cyanide. Potassic sulphate. Abnormal cyanide or nitrile.

2. The fatty acids are converted into ammonium salts and distilled with phosphoric anhydride, when the abnormal cyanides of the positive radicals which they contain, or nitriles, are produced:—

$$\left\{\begin{array}{l}C_nH_{2n+1}\\ \mathbf{C}O(N^{v}H_4O)\end{array}\right. + 2\mathbf{P}_2O_5 = \left\{\begin{array}{l}C_nH_{2n+1}\\ \mathbf{C}N'''\end{array}\right. + 4\mathbf{P}O_2Ho.$$

Ammonium salt. Phosphoric anhydride. Abnormal cyanide or nitrile. Metaphosphoric acid.

3. By the action of chloroform on an amine in the presence of an alcoholic solution of potassic hydrate, a normal cyanide is produced. These cyanides are isomeric with those obtained by the two previous processes, and appear to contain nitrogen in the pentad condition:—

$$\left\{\begin{array}{l}C_nH_{2n+1}\\ \mathbf{N}H_2\end{array}\right. + \mathbf{C}HCl_3 = 3HCl + \left\{\begin{array}{l}\mathbf{C}_nH_{2n+1}\\ \mathbf{N}C\end{array}\right..$$

Amine. Chloroform. Hydrochloric acid. Cyanide.

Reactions.—1. Treated with alcoholic solution of potash, most of the haloid ethers of the C_nH_{2n+1} series, except the cyanides, are reconverted into alcohols:—

$$C_nH_{2n+1}Cl + KHo = C_nH_{2n+1}Ho + KCl.$$

Haloid ether. Potassic hydrate. Alcohol. Potassic chloride.

2. The nitriles, or abnormal cyanides, under similar circum-

stances are converted into potassic salts of the acids which contain the positive radical of the cyanide :—

$$\underset{\text{Abnormal cyanide.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ CN'''\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\text{Potassic salt.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ COKo\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

3. The nitriles or abnormal cyanides when submitted to the action of acids yield an ammonic salt and a fatty acid :—

$$\underset{\text{Nitrile.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ CN'''\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Ammonic chloride.}}{NH_4Cl} + \underset{\text{Fatty acid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ COHo\end{matrix}\right.}.$$

4. The normal cyanides when acted on by acids behave like hydrocyanic acid (see p. 28), producing formic acid and the hydrochlorate of an amine :—

$$\underset{\text{Cyanide.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ NC'\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ COHo\end{matrix}\right.} + \underset{\text{Hydrochlorate of amine.}}{N(C_nH_{2n+1})H_3Cl}.$$

This reaction appears to take place in three stages; and in the case of phenylic cyanide the intermediate compounds have been obtained :—

$$2\underset{\text{Phenylic cyanide.}}{\left\{\begin{matrix}C_6H_5\\ NC'\end{matrix}\right.} + \underset{\text{Water}}{2OH_2} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ COHo\end{matrix}\right.} + \underset{\text{Formyl-diphenyl-diamine.}}{N_2(CH)'''(C_6H_5)_2H}.$$

$$\underset{\text{Formyl-diphenyl-diamine.}}{N_2(CH)'''(C_6H_5)_2H} + \underset{\text{Water.}}{OH_2} = \underset{\text{Phenyl formamide.}}{\left\{\begin{matrix}C_6H_5\\ N(COH)H\end{matrix}\right.} + \underset{\text{Phenylamine.}}{\left\{\begin{matrix}C_6H_5\\ NH_2\end{matrix}\right.}.$$

$$\underset{\text{Phenyl formamide.}}{\left\{\begin{matrix}C_6H_5\\ N(COH)H\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} = \underset{\text{Phenylamine.}}{\left\{\begin{matrix}C_6H_5\\ NH_2\end{matrix}\right.} + \underset{\text{Formic acid.}}{\left\{\begin{matrix}H\\ COHo\end{matrix}\right.}.$$

5. When the iodides are digested with zinc or magnesium, the radicals are either liberated or unite with the metal :—

$$\underset{\text{Iodide.}}{2C_nH_{2n+1}I} + 2Zn = \underset{\text{Organo-zinc compound.}}{Zn(C_nH_{2n+1})_2} + \underset{\text{Zincic iodide.}}{ZnI_2},$$

or

$$\underset{\text{Iodide.}}{2C_nH_{2n+1}I} + Zn = \underset{\text{Free radical.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n+1}\end{matrix}\right.} + \underset{\text{Zincic iodide.}}{ZnI_2}.$$

6. When the iodides are submitted to the action of sodic ethylate, a mixed ether (or a simple ether if $n=2$) is formed:—

$$\underset{\text{Sodic ethylate.}}{C_2H_5Nao} + \underset{\text{Iodide.}}{C_nH_{2n+1}I} = \underset{\text{Ether.}}{\left\{\begin{matrix}C_nH_{2n+1}\\ O\\ C_2H_5\end{matrix}\right.} + NaI.$$

7. The haloid ethers of the monad positive radicals are the representatives of the hydracids of mineral chemistry, and unite directly with ammonia, producing salts which, when treated with potassic hydrate, yield compound ammonias containing the basylous radical of the haloid ether in the place of one atom of hydrogen:

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Ethylic iodide.}}{EtI} = \underset{\text{Ethylammonic iodide.}}{NH_3EtI}.$$

$$\underset{\text{Ethylammonic iodide.}}{NH_3EtI} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ethylamine.}}{NEtH_2} + \underset{\text{Potassic iodide.}}{KI} + \underset{\text{Water.}}{OH_2}.$$

METHYLIC CHLORIDE.

CH_3Cl or $MeCl$.

Molecular weight $=50{\cdot}5$. *Molecular volume* ☐☐. 1 *litre of methylic chloride vapour weighs* 25·25 *criths. Boils at* $-21°$.

Preparation.—By heating together sodic chloride, methylic alcohol, and sulphuric acid:—

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Methylic alcohol.}}{MeHo} = \underset{\text{Sulphomethylic acid.}}{SO_2MeoHo} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Sulphomethylic acid.}}{SO_2MeoHo} + \underset{\text{Sodic chloride.}}{NaCl} = \underset{\text{Methylic chloride.}}{MeCl} + \underset{\text{Hydric sodic sulphate.}}{SO_2HoNao}.$$

Reaction.—By the action of chlorine, methylic chloride produces three substitution derivatives:—

				Boiling-point.
Monochlorinated	methylic	chloride,	CH_2Cl_2.	31°
Dichlorinated	„	„	$CHCl_3$.	60°·8
Trichlorinated	„	„	CCl_4.	78°

Chloroform, acted on by powdered zinc and a solution of ammonia, produces methylenic dichloride, boiling between 40° and 42°. It seems to differ from monochlorinated methylic chloride, which is said to boil at 31°.

CHLOROFORM, *Dichlorinated Methylic Chloride.*

$CHCl_3$.

Molecular weight =119·5. *Molecular volume* ☐☐. 1 *litre of chloroform vapour weighs* 59·75 *criths. Sp. gr.* 1·48. *Boils at* 60°·8.

Preparation.—This compound is manufactured in large quantities by heating alcohol with a solution of calcic chlorohypochlorite (*chloride of lime*). It may also be made by treating methylic alcohol in the same manner. For the reaction see p. 57.

Reactions.—1. Chloroform is transformed into potassic formate by boiling with alcoholic potash:—

$$\underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Potassic hydrate.}}{4KHo} = \underset{\text{Potassic formate.}}{CHOKo} + \underset{\text{Potassic chloride.}}{3KCl} + \underset{\text{Water.}}{2OH_2}.$$

2. When acted upon by chlorine in the presence of sunlight, the hydrogen of chloroform is displaced by chlorine, and carbonic tetrachloride (CCl_4) formed.

ETHYLIC CHLORIDE.

C_2H_5Cl or EtCl.

Molecular weight =64·5. *Molecular volume* ◻◻. 1 *litre of ethylic chloride vapour weighs* 32·25 *criths. Sp. gr.* 0·874. *Boils at* 11°·5.

Preparation.—Ethylic alcohol is saturated with hydrochloric acid, and digested in sealed tubes at 100° for one or two hours, when the mixture separates into two layers, the upper one being the ethylic chloride:—

$$\underset{\text{Alcohol.}}{EtHo} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylic chloride.}}{EtCl} + \underset{\text{Water.}}{OH_2}.$$

ETHYLIC IODIDE.

C_2H_5I or EtI.

Molecular weight =156. *Molecular volume* ◻◻. 1 *litre of ethylic iodide vapour weighs* 78 *criths. Sp. gr.* 1·9461. *Boils at* 72°·2.

Preparation.—By placing in a retort two parts by weight of alcohol and one of amorphous phosphorus, and then introducing five parts of iodine and distilling in a water-bath:—

$$\underset{\text{Alcohol.}}{3C_2H_5Ho} + P + I_3 = \underset{\text{Ethylic iodide.}}{3C_2H_5I} + \underset{\text{Phosphorous acid.}}{POHHo_2}.$$

Reaction.—Ethylic iodide, when heated with water in a sealed tube, produces ether and hydriodic acid:—

$$\underset{\text{Ethylic iodide.}}{2C_2H_5I} + \underset{\text{Water.}}{OH_2} = \underset{\text{Ether.}}{\left\{\begin{matrix} C_2H_5 \\ O \\ C_2H_5. \end{matrix}\right.} + \underset{\text{Hydriodic acid.}}{2HI}.$$

The methylic and amylic iodides are similar liquids, and obtained by analogous processes; the methylic iodide, CH_3I, has the sp. gr. 2·237, and boils at 42° C. Amylic iodide, $C_5H_{11}I$, has the sp. gr. 1·511, and boils at 146°.

The haloid compounds of the allylic and phenylic series are of comparatively little importance.

HALOID ETHERS OF THE DYAD POSITIVE RADICALS.

I. *Haloid ethers of the form* $C_nH_{2n}HoCl$.

Preparation.—These ethers are prepared by the action of the hydracids on the glycols. The following will serve as examples of this class:—

Ethylenic chlorhydrate or chlorhydric glycol $\left\{\begin{matrix} CH_2Ho \\ CH_2Cl \end{matrix}\right.$.

Ethylenic iodhydrate or iodhydric glycol ... $\left\{\begin{matrix} CH_2Ho \\ CH_2I \end{matrix}\right.$.

Treated with potassic hydrate, both these bodies give ethylenic oxide, as previously described (p. 90).

II. *Haloid ethers of the form* $C_nH_{2n}Cl_2$.

Preparation.—These ethers are generally formed by the direct union of the dyad radicals with the negative elements.

The following list comprises the chief members of this class:—

		Boiling-point.
Methylenic chloride.........	CH_2Cl_2	40°
„ iodide	CH_2I_2	181°
Ethylenic chloride	$C_2H_4Cl_2$	85°
„ bromide	$C_2H_4Br_2$	129°

		Boiling-point.
Ethylenic iodide	$C_2H_4I_2$	
Propylenic chloride	$C_3H_6Cl_2$	103°
„ bromide	$C_3H_6Br_2$	144°
„ iodide	$C_3H_6I_2$	——
Butylenic chloride	$C_4H_8Cl_2$	127°
„ bromide	$C_4H_8Br_2$	160°
Amylenic chloride	$C_5H_{10}Cl_2$	——
„ bromide	$C_5H_{10}Br_2$	175°

By the action of potassium, sodium, or zinc, the radicals are again liberated, except in the case of the methylene compounds. The bromides are the most important members of the series.

ETHYLENIC BROMIDE.

$$C_2H_4Br_2 \text{ or } \left\{\begin{array}{l} CH_2Br \\ CH_2Br \end{array}\right. \text{ or } Et''Br_2.$$

Molecular weight =188. *Molecular volume* ☐☐. 1 *litre of ethylenic bromide vapour weighs* 94 *criths. Sp. gr.* 2·16. *Fuses at* −18°. *Boils at* 129°.

Preparation.—By agitating bromine and water with ethylene.

Reactions.—1. Boiled with alcoholic potash it yields bromethylene or vinylic bromide:—

$$\underset{\substack{\text{Ethylenic}\\\text{bromide.}}}{C_2H_4Br_2} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Vinylic bromide}\\\text{or bromethylene.}}}{C_2H_3Br} + \underset{\substack{\text{Potassic}\\\text{bromide.}}}{KBr} + \underset{\text{Water.}}{OH_2}.$$

2. Heated with an alcoholic solution of potassic acetate, it yields monacetic glycol.

$$\underset{\substack{\text{Ethylenic}\\\text{bromide.}}}{\left\{\begin{array}{l} CH_2Br \\ CH_2Br \end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{acetate.}}}{2CMeOKo} + \underset{\text{Water.}}{OH_2} = \underset{\text{Monacetic glycol.}}{\left\{\begin{array}{l} CH_2\text{-}O\text{-}CMeO \\ CH_2Ho \end{array}\right.}$$

$$+ \underset{\substack{\text{Acetic}\\\text{acid}}}{CMeOHo} + \underset{\substack{\text{Potassic}\\\text{bromide.}}}{2KBr}.$$

ETHYLENIC CYANIDE, *Ethylenic Nitrile.*

$$\left\{\begin{matrix} \mathrm{CH_2Cy} \\ \mathrm{CH_2Cy} \end{matrix}\right. = \mathrm{C_2H_4Cy_2}.$$

***Fuses at* 37°.**

Preparation.—By heating ethylenic bromide with potassic cyanide to 100° for sixteen hours:—

$$\underset{\text{Ethylenic bromide.}}{\left\{\begin{matrix} \mathrm{CH_2Br} \\ \mathrm{CH_2Br} \end{matrix}\right.} + \underset{\text{Potassic cyanide.}}{\mathrm{2CN'''K}} = \underset{\text{Ethylenic nitrile.}}{\left\{\begin{matrix} \mathrm{CH_2(CN''')} \\ \mathrm{CH_2(CN''')} \end{matrix}\right.} + \underset{\text{Potassic bromide.}}{\mathrm{2KBr}}.$$

Reaction.—When boiled with alcoholic potash, ethylenic nitrile or abnormal cyanide yields potassic succinate:—

$$\underset{\text{Ethylenic nitrile.}}{\left\{\begin{matrix} \mathrm{CH_2(CN''')} \\ \mathrm{CH_2(CN''')} \end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{2KHo}} + \underset{\text{Water.}}{\mathrm{2OH_2}} = \underset{\text{Potassic succinate.}}{\left\{\begin{matrix} \mathrm{CH_2(COKo)} \\ \mathrm{CH_2(COKo)} \end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathrm{2NH_3}}.$$

HALOID ETHERS OF THE TRIAD POSITIVE RADICALS.

I. of the form $C_nH_{2n-1}Ho_2Cl$.

		Boiling-point.
Chlorhydrin .	$\left\{\begin{matrix} \mathrm{CH_2Ho} \\ \mathrm{CHCl} \\ \mathrm{CH_2Ho} \end{matrix}\right.$	227°.
Bromhydrin ...	$\left\{\begin{matrix} \mathrm{CH_2Ho} \\ \mathrm{CHBr} \\ \mathrm{CH_2Ho} \end{matrix}\right.$	180° *in vacuo.*

II. of the form $C_nH_{2n-1}HoCl_2$.

Dichlorhydrin...	$\left\{\begin{matrix} \mathrm{CH_2Cl} \\ \mathrm{CHHo} \\ \mathrm{CH_2Cl} \end{matrix}\right.$	180°.

III. of the form $C_nH_{2n-1}Cl_3$.

Boiling-point.

$$\text{Trichlorhydrin..}\left\{\begin{array}{l}CH_2Cl\\ CHCl\\ CH_2Cl\end{array}\right. \text{...... ..... } 155^\circ.$$

IV. Of the form $C_nH_{2n-1}OCl$.

$$\begin{array}{r}\text{Hydrochloric}\\ \text{glycide or epi-}\\ \text{chlorhydrin ...}\end{array}\left\{\begin{array}{l}CH_2\\ CH\\ CH_2Cl\end{array}\right.\!\!\!\begin{array}{l}\}O\\ \\ \\ \end{array} \text{...........} \ 118^\circ.$$

Preparation.—The ethers of the first three forms are obtained by the action of the hydracids upon glycerin; whilst those of the fourth are produced by the action of alkalies upon the second form of compounds.

CHAPTER XV.

THE ALDEHYDES.

THESE compounds are intermediate between the alcohols and the acids. They are formed from alcohols by the abstraction of hydrogen; hence the name, which is an abbreviation of *alcohol dehydrogenatum.*

Three series of aldehydes are known, corresponding to the three series of monacid alcohols, viz.:—

A. Aldehydes derived from $C_nH_{2n+1}Ho$ alcohols.
B. „ „ „ $C_nH_{2n-1}Ho$ „
C. „ „ „ $C_nH_{2n-7}Ho$ „

Preparation.—1. The aldehydes are formed by the oxidation of the alcohols; ethylic alcohol, for instance, yields acetic aldehyde:—

$$\underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.} + O = \underset{\substack{\text{Acetic}\\\text{aldehyde *.}}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

2. Aldehydes are also formed by distilling a mixture of molecular quantities of the potassic salt of a fatty acid and of potassic formate :—

$$\underset{\substack{\text{Potassic}\\\text{acetate.}}}{\left\{\begin{array}{l}CH_3\\COKo\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{formate.}}}{\left\{\begin{array}{l}H\\COKo\end{array}\right.} = \underset{\substack{\text{Acetic}\\\text{aldehyde.}}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{carbonate.}}}{COKo_2}.$$

This is an important reaction, as by its means the series of fatty acids can be ascended; for the aldehyde may next be transformed into an alcohol by nascent hydrogen then the alcohol converted into an abnormal cyanide or nitrile, which by treatment with potassic hydrate gives the potassic salt of the next higher acid. Thus :—

$$\underset{\substack{\text{Acetic}\\\text{aldehyde.}}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} + H_2 = \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.};$$

$$\underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2Ho_2} = \underset{\substack{\text{Sulphovinic}\\\text{acid.}}}{SO_2HoEto} + \underset{\text{Water.}}{OH_2};$$

$$\underset{\substack{\text{Sulphovinic}\\\text{acid.}}}{SO_2HoEto} + \underset{\substack{\text{Potassic}\\\text{cyanide.}}}{CN'''K} = \underset{\substack{\text{Hydric potassic}\\\text{sulphate.}}}{SO_2KoHo} + \underset{\substack{\text{Ethylic}\\\text{nitrile.}}}{\left\{\begin{array}{l}CMeH_2\\CN'''\end{array}\right.};$$

$$\underset{\substack{\text{Ethylic}\\\text{nitrile.}}}{\left\{\begin{array}{l}CMeH_2\\CN'''\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Potassic}\\\text{propionate.}}}{\left\{\begin{array}{l}CMeH_2\\COKo\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

Starting again with potassic propionate, instead of potassic acetate, the same series of reactions can be performed, resulting in potassic butyrate, and so on.

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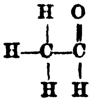


Reactions.—1. By direct absorption of oxygen, the aldehydes are transformed into the corresponding acids:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + O = \underset{\text{Acid.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COHo\end{array}\right.}.$$

2. Also heated with ammoniacal solution of argentic oxide, the aldehydes are converted into acids, metallic silver being deposited:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + \underset{\text{Argentic oxide.}}{OAg_2} = \underset{\text{Acid.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COHo\end{array}\right.} + Ag_2.$$

3. When heated with potassic hydrate, the aldehydes yield the potassic salts of the corresponding acids, with evolution of hydrogen:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{salt.}}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COKo\end{array}\right.} + H_2.$$

4. Treated with nascent hydrogen, they are converted into the corresponding alcohols:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + H_2 = \underset{\text{Alcohol.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\CH_2Ho\end{array}\right.}.$$

5. Most aldehydes combine directly with ammonia, forming crystalline compounds:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3} = \underset{\substack{\text{Ammonium}\\\text{compound.}}}{\left\{\begin{array}{l}C_nH_{2n+1}\\CO(NH_4)\end{array}\right.}.$$

6. Aldehydes also combine with the alkaline hydric sulphites, producing crystalline compounds:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right.} + \underset{\substack{\text{Hydric potassic}\\\text{sulphite.}}}{SOKoHo} = SOKoHo,\left\{\begin{array}{l}C_nH_{2n+1}\\COH\end{array}\right..$$

A. *ALDEHYDES DERIVED FROM THE* $C_nH_{2n+1}Ho$ *SERIES OF ALCOHOLS.*

The following are known:—

		Fusing-point.	Boiling-point.
Formic aldehyde ...	$\left\{\begin{matrix}H\\COH\end{matrix}\right.$	——	——
Acetic aldehyde	$\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.$	——	21°.
Propionic aldehyde..	$\left\{\begin{matrix}CMeH_2\\COH\end{matrix}\right.$ or $\left\{\begin{matrix}C(CH_3)H_2\\COH\end{matrix}\right.$	——	(40°-45°).
Butyric aldehyde ...	$\left\{\begin{matrix}CEtH_2\\COH\end{matrix}\right.$ or $\left\{\begin{matrix}C(C_2H_5)H_2\\COH\end{matrix}\right.$	——	(68°-75°).
Valeric aldehyde ...	$\left\{\begin{matrix}CPrH_2\\COH\end{matrix}\right.$ or $\left\{\begin{matrix}C(C_3H_7)H_2\\COH\end{matrix}\right.$	——	93°.
Œnanthic aldehyde..	$\left\{\begin{matrix}CAyH_2\\COH\end{matrix}\right.$ or $\left\{\begin{matrix}C(C_5H_{11})H_2\\COH\end{matrix}\right.$	below −12°.	152°.
Capric aldehyde......	$\left\{\begin{matrix}C(C_8H_{17})H_2\\COH\end{matrix}\right.$	− 2°.	228°?
Euodic aldehyde......	$\left\{\begin{matrix}C(C_9H_{19})H_2\\COH\end{matrix}\right.$	+ 7°.	213°.
Lauric aldehyde.....	$\left\{\begin{matrix}C(C_{10}H_{21})H_2\\COH\end{matrix}\right.$	——	232°.
Palmitic aldehyde ...	$\left\{\begin{matrix}C(C_{14}H_{29})H_2\\COH\end{matrix}\right.$	52°.	

ACETIC ALDEHYDE, *Aldehyde.*

$$\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.$$

Molecular weight =44. *Molecular volume* ☐☐. 1 *litre of aldehyde vapour weighs* 22 *criths. Sp. gr.* =0·79. *Boils at* 21°·8.

Preparation.—1. By oxidizing alcohol with chromic acid, chlorine water, or manganic oxide and sulphuric acid:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} + O = \underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

2. By oxidation, casein, fibrin, and albumen also yield aldehyde.

3. Aldehyde is formed when the vapour of alcohol or ether is passed through a tube heated to dull redness.

Reactions.—1. It gradually absorbs oxygen from the air, forming acetic acid, into which it is also readily converted by oxidizing agents:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COH}\end{matrix}\right.} + \mathrm{O} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHo}\end{matrix}\right.}$$

2. It reduces silver salts, depositing lustrous metallic silver on the sides of the vessel.

3. By the action of phosphoric chloride on aldehyde, ethylidenic dichloride is produced:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Phosphoric chloride}}{\mathrm{PCl_5}} = \underset{\text{Ethylidenic dichloride.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CHCl_2}\end{matrix}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{\mathrm{POCl_3}}.$$

4. When submitted to the action of potassium, one atom of hydrogen is substituted by an atom of the metal, the compound

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COK}\end{matrix}\right.$$

being formed.

5. Hydrocyanic acid transforms aldehyde into alanin:—

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COH}\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathrm{NCH}} + \underset{\text{Water.}}{\mathrm{OH_2}} = \underset{\text{Alanin.}}{\left\{\begin{matrix}\mathrm{CMeH(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right.}.$$

By the action of nitrous anhydride, alanin or lactamic acid is converted into lactic acid:—

$$2\underset{\text{Alanin.}}{\left\{\begin{matrix}\mathrm{CMeH(N'''H_2)}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Nitrous anhydride.}}{\mathrm{N_2O_3}} = 2\underset{\text{Lactic acid.}}{\left\{\begin{matrix}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{matrix}\right.} + 2\mathrm{N_2} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

There are three isomeric modifications of aldehyde:—

Metaldehyde, crystalline, subliming at 120°.
Paraldehyde, liquid, boiling at 125°.
Elaldehyde, crystalline, fusing at 2°, boiling at 94°.

By the action of chlorine upon alcohol, trichlor-aldehyde is formed containing 3 atoms of chlorine in the place of 3 atoms of methylic hydrogen. It is named *chloral*,

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}OH\end{array}\right..$$

This compound immediately unites with one molecule of water, forming *chloral hydrate*, which has the following constitutional formula:—

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}HHo_2\end{array}\right..$$

In the same operation *chloral alcoholate* is generally produced. Its constitution is expressed by the following formula:—

$$\left\{\begin{array}{l}\mathbf{C}Cl_3\\ \mathbf{C}HEtoHo\end{array}\right..$$

B. *ALDEHYDES DERIVED FROM THE* $C_nH_{2n-1}Ho$ *ALCOHOLS.*

ACROLEIN. *Acrylic Aldehyde.*

$$\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right..$$

Molecular weight =56. *Molecular volume* $\square\!\square$. 1 *litre of acrolein vapour weighs* 28 *criths. Boils at* 52° 4.

Preparation.—1. By the action of phosphoric anhydride or of sulphuric acid on glycerin:—

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}HHo\\ \mathbf{C}H_2Ho\end{array}\right.} = \underset{\text{Water}}{2\mathbf{O}H_2} + \underset{\text{Acrolein}}{\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right.}.$$

2. By the oxidation of allylic alcohol:—

$$\underset{\text{Allylic alcohol}}{\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}H_2Ho\end{array}\right.} + \mathrm{O} = \underset{\text{Acrolein.}}{\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OH\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

3 By the action of heat on the product of the union of acetone with bromine:—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}\mathbf{C}OMe\\ \mathbf{C}H_3\end{matrix}\right.} + Br_2 = \left\{\begin{matrix}\mathbf{C}MeBr_2\\ \mathbf{C}H_2Ho\end{matrix}\right. :$$

$$\left\{\begin{matrix}\mathbf{C}MeBr_2\\ \mathbf{C}H_2Ho\end{matrix}\right. = \underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathbf{C}Me''H\\ \mathbf{C}OH\end{matrix}\right.} + \underset{\text{Hydrobromic acid.}}{2HBr.}$$

Reaction.—By oxidation, acrolein yields acrylic acid:—

$$\underset{\text{Acrolein.}}{\left\{\begin{matrix}\mathbf{C}Me''H\\ \mathbf{C}OH\end{matrix}\right.} + O = \underset{\text{Acrylic acid.}}{\left\{\begin{matrix}\mathbf{C}Me''H\\ \mathbf{C}OHo\end{matrix}\right.} \cdot$$

C. *ALDEHYDES DERIVED FROM THE* $C_nH_{2n-7}Ho$ *ALCOHOLS.*

		Boiling-point.
Benzoic aldehyde ……	$\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}OH\end{matrix}\right.$	…180°.
Cuminic aldehyde . …	$\left\{\begin{matrix}\mathbf{C}_9H_{11}\\ \mathbf{C}OH\end{matrix}\right.$	…229°·4.

BENZOIC ALDEHYDE, *Oil of Bitter Almonds, Hydride of Benzoyl.*

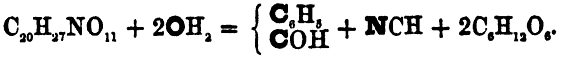
$$\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}OH\end{matrix}\right. \cdot$$

Molecular weight =106. *Molecular volume* $\square\square$. 1 *litre of benzoic aldehyde vapour weighs* 53 *criths. Sp. gr.* 1·043. *Boils at* 180°.

Preparation.—1. By the oxidation of amygdalin by nitric acid, and by the action of a mixture of manganic oxide and sulphuric acid on albumen, fibrin, casein, and gelatin.

2. By digesting bitter almonds with water for five or six hours at 30°–40°. The synaptase present acts as a ferment on

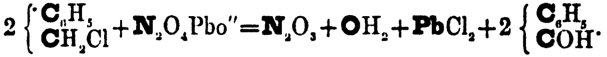
the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid:—



$$C_{20}H_{27}NO_{11} + 2OH_2 = \left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right. + NCH + 2C_6H_{12}O_6.$$

Amygdalin. Water. Benzoic aldehyde. Hydrocyanic acid. Glucose.

3. By digesting together plumbic nitrate, water, and benzylic chloride (chlorotoluol), benzoic aldehyde is formed:—

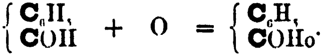


$$2\left\{\begin{matrix}C_6H_5\\CH_2Cl\end{matrix}\right. + N_2O_4Pbo'' = N_2O_3 + OH_2 + PbCl_2 + 2\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right..$$

Benzylic chloride. Plumbic nitrate. Nitrous anhydride. Water. Plumbic chloride. Benzoic aldehyde.

The benzylic chloride is prepared by passing chlorine into the vapour of boiling toluol.

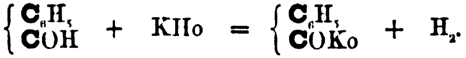
Reactions.—1. When exposed to the air, benzoic aldehyde absorbs oxygen and is converted into benzoic acid:—



$$\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right. + O = \left\{\begin{matrix}C_6H_5\\COHo\end{matrix}\right..$$

Benzoic aldehyde. Benzoic acid.

2. Heated with solid potassic hydrate, it gives hydrogen and potassic benzoate:—



$$\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right. + KHo = \left\{\begin{matrix}C_6H_5\\COKo\end{matrix}\right. + H_2.$$

Benzoic aldehyde. Potassic hydrate. Potassic benzoate.

CHAPTER XVI.

THE ACIDS.

The acids form the most numerous family of organic compounds.

Many of them are contained in plants in the free state, or in combination as metallic or ethereal salts.

Others are produced by the action of chemical agents on various organic substances.

Some are formed in the animal organism, as, for instance, formic, paralactic, oleic, and stearic acids.

The organic acids are divided into three great classes, according to their basicity:—

1. Monobasic acids.
2. Dibasic acids.
3. Tribasic acids.

The basicity of organic acids is determined by the following simple law:—*an organic acid containing* n *semimolecules of oxatyl is* n-*basic.*

MONOBASIC ACIDS.

The monobasic acids, which always contain a single semimolecule of oxatyl ($\mathbf{C}OHo$), include the six following series:—

	General formulæ.
1. Acetic or fatty series	$\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{matrix}\right.$.
2. Acrylic or oleic series	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n})''(C_mH_{2m+1})\\ \mathbf{C}OHo\end{matrix}\right.$.
3. Lactic series	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OHo\end{matrix}\right.$.
4. Pyruvic series	$\left\{\begin{matrix}\mathbf{C}O(C_nH_{2n+1})\\ \mathbf{C}OHo\end{matrix}\right.$.
5. Glyoxylic series..............	$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})Ho_2\\ \mathbf{C}OHo\end{matrix}\right.$.
6. Benzoic or aromatic series	$\left\{\begin{matrix}\mathbf{C}_nH_{2n-7}\\ \mathbf{C}OHo\end{matrix}\right.$.

The 1st, 2nd, 3rd, 5th, and 6th of these series may be regarded as the derivatives from corresponding series of alcohols.

1. The Acetic series from the Methyl series of alcohols.
2. „ Acrylic „ „ Vinyl „ „
3. „ Lactic „ „ Glycol „ „
5. „ Glyoxylic „ „ Glycerin „ „
6. „ Benzoic „ „ Phenyl „ „

The acids of the first, second, fourth, and sixth series are termed *monohydric* as well as monobasic; whilst the acids of the third series are termed *dihydric* and monobasic, indicating their origin from the dihydric alcohols, and that they contain two semimolecules of hydroxyl, one of which is in the oxatyl or negative part, and the other in the positive part of the molecule. The hydrogen of the latter hydroxyl may be displaced by highly positive metals, in the same manner as the hydrogen of the hydroxyl in alcohols; but it cannot be displaced by double decomposition with bases, in the same manner as the hydrogen in the oxatyl may be substituted.

The acids of the fifth series are termed *trihydric* and monobasic, indicating that they are derived from the trihydric alcohols, and that they contain, besides the hydroxyl in the oxatyl, two other semimolecules of hydroxyl in the positive part of the molecule.

1. *ACETIC OR FATTY SERIES OF ACIDS.*

General formula... $\left\{\begin{array}{l}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{array}\right.$.

These acids may be conveniently arranged under three divisions, viz.:—

A. Normal acids.

General formula .. $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}OHo\end{array}\right.$.

B. Secondary acids.

General formula... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2H\\ \mathbf{C}OHo\end{array}\right.$.

C. Tertiary acids.

General formula... $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_3\\ \mathbf{C}OHo\end{array}\right.$.

A. *NORMAL ACIDS OF THE ACETIC OR FATTY SERIES.*

General formula... $\begin{cases}\mathbf{C}(C_nH_{2n+1})H_2 \\ \mathbf{C}OHo\end{cases}$.

In formic acid, which is generally considered to be the first term of this division, the radical $\mathbf{C}(C_nH_{2n+1})H_2$ is replaced by H; and in acetic acid the value of $n=0$. In reference to the following list of normal fatty acids, it must be borne in mind that the normal character has not been established in the case of those members which possess a higher molecular weight than œnanthylic acid:—

				Fusing point.	Boiling-point.
Formic acid			$\begin{cases}H \\ \mathbf{C}OHo\end{cases}$	+1°.	100°.
Acetic acid	$\begin{cases}Me \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}H_3 \\ \mathbf{C}OHo\end{cases}$	+17°.	117°.
Propionic acid	$\begin{cases}\mathbf{C}MeH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(CH_3)H_2 \\ \mathbf{C}OHo\end{cases}$	——	141°.
Butyric acid	$\begin{cases}\mathbf{C}EtH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(C_2H_5)H_2 \\ \mathbf{C}OHo\end{cases}$	below −20°.	161°.
Valeric acid	$\begin{cases}\mathbf{C}PrH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(C_3H_7)H_2 \\ \mathbf{C}OHo\end{cases}$	——	175°.
Isopropacetic acid	$\begin{cases}\mathbf{C}\beta PrH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(CMe_2H)H_2 \\ \mathbf{C}OHo\end{cases}$	——	175°.
Caproic acid	$\begin{cases}\mathbf{C}BuH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(C_4H_9)H_2 \\ \mathbf{C}OHo\end{cases}$	+5°.	198°.
Œnanthylic acid	$\begin{cases}\mathbf{C}AyH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(C_5H_{11})H_2 \\ \mathbf{C}OHo\end{cases}$	——	212°.
Caprylic acid	$\begin{cases}\mathbf{C}CpH_2 \\ \mathbf{C}OHo\end{cases}$	or	$\begin{cases}\mathbf{C}(C_6H_{13})H_2 \\ \mathbf{C}OHo\end{cases}$	+14°.	236°.
Pelargonic acid			$\begin{cases}\mathbf{C}(C_7H_{15})H_2 \\ \mathbf{C}OHo\end{cases}$	+18°?	260°.

		Fusing-point.
Capric acid	$\left\{\begin{array}{l}\mathbf{C}(C_8H_{17})H_2\\ OHo\end{array}\right.$	27°·2(30°).
Lauric acid	$\left\{\begin{array}{l}\mathbf{C}(C_{10}H_{21})H_2\\ \mathbf{C}OHo\end{array}\right.$	43°·6.
Myristic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{12}H_{25})H_2\\ \mathbf{C}OHo\end{array}\right.$	53°·8.
Palmitic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{14}H_{29})H_2\\ \mathbf{C}OHo\end{array}\right.$	62°.
Margaric acid	$\left\{\begin{array}{l}\mathbf{C}(C_{15}H_{31})H_2\\ \mathbf{C}OHo\end{array}\right.$	59°·9 ?
Stearic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{16}H_{33})H_2\\ \mathbf{C}OHo\end{array}\right.$	69°·2.
Arachidic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{18}H_{37})H_2\\ \mathbf{C}OHo\end{array}\right.$	75°.
Behenic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{20}H_{41})H_2\\ \mathbf{C}OHo\end{array}\right.$	76°.
Hyœnasic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{23}H_{47})H_2\\ \mathbf{C}OHo\end{array}\right.$	77°.
Cerotic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{25}H_{51})H_2\\ \mathbf{C}OHo\end{array}\right.$	78°.
Melissic acid	$\left\{\begin{array}{l}\mathbf{C}(C_{28}H_{57})H_2\\ \mathbf{C}OHo\end{array}\right.$	88°.

Occurrence.—The greater number of the acids of this series are met with already formed in nature, some in the free state, as formic acid in ants and nettles, valeric acid in the valerian root, pelargonic acid in the essential oil of the *Pelargonium roseum*, and cerotic acid in bee's-wax.

Others are met with as the ethereal salts of monohydric alcohols. Thus spermaceti is cetylic palmitate, and chinese wax cerylic cerotate.

A large number exist as natural fats in the form of the ethereal salts of glycerin: this is the case with butyric, palmitic, and stearic acids, which, united with glycerin, form respectively butyrin, palmitin, and stearin.

Formation.—1. By the oxidation of the normal alcohols of the methyl series, as in the conversion of alcohol into acetic acid by heating it with a solution of chromic acid:—

$$\underset{\text{Alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right.} + O_2 = \underset{\substack{\text{Acetic}\\\text{acid.}}}{\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

2. By the action of alkalies or acids upon the nitriles or abnormal cyanides of the C_nH_{2n+1} series of radicals:—

$$\underset{\text{Nitrile.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CN'''\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Potassic}\\\text{salt.}}}{\left\{\begin{matrix}C_nH_{2n+1}\\COKo\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3};$$

and

$$\underset{\text{Nitrile.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CN'''\end{matrix}\right.} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Acid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COHo\end{matrix}\right.} + \underset{\substack{\text{Ammonic}\\\text{chloride.}}}{NH_4Cl}.$$

Instances of these reactions are seen in the treatment of ethylic nitrile by a boiling solution of potassic hydrate, when it is converted into potassic propionate, ammonia being evolved, thus—

$$\underset{\substack{\text{Ethylic}\\\text{nitrile.}}}{\left\{\begin{matrix}CMeH_2\\CN'''\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Potassic}\\\text{propionate.}}}{\left\{\begin{matrix}CMeH_2\\COKo\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3};$$

and in the conversion of ethylic nitrile, by the action of hydrochloric acid, into ammonic chloride and propionic acid—

$$\underset{\substack{\text{Ethylic}\\\text{nitrile.}}}{\left\{\begin{matrix}CMeH_2\\CN'''\end{matrix}\right.} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} + \underset{\text{Water.}}{2OH_2} = \underset{\substack{\text{Propionic}\\\text{acid.}}}{\left\{\begin{matrix}CMeH_2\\COHo\end{matrix}\right.} + \underset{\substack{\text{Ammonic}\\\text{chloride.}}}{NH_4Cl}.$$

3. By the action of the potassium or sodium compounds of the C_nH_{2n+1} radicals upon carbonic anhydride—

$$\begin{array}{ccccc} CO_2 & + & C_nH_{2n+1}Na & = & \left\{\begin{matrix} C_nH_{2n+1} \\ CONao \end{matrix}\right., \\ \text{Carbonic anhydride.} & & \text{Sodium compound.} & & \text{Sodic salt.} \end{array}$$

as, for example, in the formation of sodic propionate by the absorption of carbonic anhydride by sodic ethide:—

$$\begin{array}{ccccc} CO_2 & + & CMeH_2Na & = & \left\{\begin{matrix} CMeH_2 \\ CONao \end{matrix}\right.. \\ \text{Carbonic anhydride.} & & \text{Sodic ethide.} & & \text{Sodic propionate.} \end{array}$$

4. By the oxidation of aldehydes—

$$\begin{array}{ccccc} \left\{\begin{matrix} C_nH_{2n+1} \\ COH \end{matrix}\right. & + & O & = & \left\{\begin{matrix} C_nH_{2n+1} \\ COHo \end{matrix}\right., \\ \text{Aldehyde.} & & & & \text{Acid.} \end{array}$$

as in the conversion of acetic aldehyde into acetic acid by the absorption of atmospheric oxygen:—

$$\begin{array}{ccccc} \left\{\begin{matrix} CH_3 \\ COH \end{matrix}\right. & + & O & = & \left\{\begin{matrix} CH_3 \\ COHo \end{matrix}\right.. \\ \text{Acetic aldehyde.} & & & & \text{Acetic acid.} \end{array}$$

Besides these reactions of general application, there are numerous special methods for the production of certain members of this series. In most of these methods, however, the reactions cannot be clearly traced.

Thus, by the oxidation of albumen, fibrin, casein, and other similar substances, there are produced formic, acetic, propionic, butyric, valeric, and caproic acids.

Propionic and butyric acids are produced in some kinds of fermentation; and acetic acid is obtained by the destructive distillation of wood and other similar substances.

Relations of the Normal Fatty Acids to the C_nH_{2n+1} *Series of Radicals.*

1. When these acids are submitted to the action of nascent oxygen evolved by electrolysis, the negative radical oxatyl is converted into carbonic anhydride and water, the positive radical being set at liberty :—

$$2\underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{matrix}\right.} + O = \underset{\substack{\text{Positive}\\ \text{radical}}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n+1}\end{matrix}\right.} + \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{2\mathbf{CO}_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

On electrolyzing a solution of potassic valerate, hydric potassic carbonate and the normal radical butyl are formed :—

$$2\underset{\substack{\text{Potassic}\\ \text{valerate.}}}{\left\{\begin{matrix}\mathbf{C}_4H_9\\ \mathbf{C}OKo\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} + O = \underset{\text{Butyl.}}{\left\{\begin{matrix}\mathbf{C}_4H_9\\ \mathbf{C}_4H_9\end{matrix}\right.} + \underset{\substack{\text{Hydric potassic}\\ \text{carbonate.}}}{2\mathbf{C}OHoKo}.$$

2. When the ammonic salts of these acids are heated with phosphoric anhydride, they are converted into the nitriles or abnormal cyanides of the radicals of the C_nH_{2n+1} series—

$$\underset{\text{Ammonic salt.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}O(N^vH_4O)\end{matrix}\right.} + \underset{\substack{\text{Phosphoric}\\ \text{anhydride.}}}{2\mathbf{P}_2O_5} = \underset{\text{Nitrile}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\substack{\text{Metaphosphoric}\\ \text{acid.}}}{4\mathbf{P}O_2Ho},$$

as in the transformation of ammonic acetate into methylic nitrile by distillation with phosphoric anhydride :—

$$\underset{\substack{\text{Ammonic}\\ \text{acetate.}}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O(N^vH_4O)\end{matrix}\right.} + \underset{\substack{\text{Phosphoric}\\ \text{anhydride.}}}{2\mathbf{P}_2O_5} = \underset{\substack{\text{Methylic}\\ \text{nitrile.}}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}N'''\end{matrix}\right.} + \underset{\substack{\text{Metaphosphoric}\\ \text{acid.}}}{4\mathbf{P}O_2Ho}.$$

These abnormal cyanides are converted into monohydric alcohols by Mendius's reaction (see p. 55).

From the alcohols so obtained, the C_nH_{2n+1} radicals are isolated as described at page 53.

Relations of the Normal Fatty Acids to the $C_nH_{2n+1}Ho$ *Series of Alcohols.*

1. By oxidation the normal alcohols yield these acids, as above shown.

2. Conversely, the normal fatty acids can be converted into the $C_nH_{2n+1}Ho$ alcohols,—

1st, by Mendius's reaction (see p. 55);

2nd, by Piria and Wurtz's reactions, viz.:—

Distillation of the potassic salt of the fatty acid with an equivalent quantity of potassic formate, by which the acid is converted into the aldehyde,

$$\underset{\text{Potassic salt.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COKo\end{matrix}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{matrix}H\\COKo\end{matrix}\right.} = \underset{\text{Aldehyde.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COH\end{matrix}\right.} + \underset{\text{Potassic carbonate.}}{COKo_2},$$

and subsequent treatment of the aldehyde by nascent hydrogen,

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COH\end{matrix}\right.} + H_2 = \underset{\text{Normal alcohol.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CH_2Ho\end{matrix}\right.}.$$

3. By the action of sodium amalgam upon a mixture of the acid and chloracid:—

$$3\underset{\text{Acid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COHo\end{matrix}\right.} + \underset{\text{Chloracid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COCl\end{matrix}\right.} + 2Na_2 = 3\underset{\text{Sodic salt.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CONao\end{matrix}\right.}$$

$$+ \underset{\text{Alcohol.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CH_2Ho\end{matrix}\right.} + NaCl.$$

The anhydride of the acid is also formed and converted, by the nascent hydrogen evolved by the action of the sodium upon the acid, into alcohol.

Relations of the Normal Fatty Acids to each other. Ascent of the Series.

If the hydrogen constituting the positive part of formic acid were substituted successively by methyl, ethyl, &c., the whole series of normal fatty acids would be obtained :—

$$\text{Formic acid}\ldots\ldots\ldots \left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

$$\text{Acetic acid}\ \ldots\ldots\ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

$$\text{Propionic acid}\ \ldots \left\{\begin{array}{l}\mathbf{C}_2\mathrm{H}_5\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

$$\text{Butyric acid}\ \ldots . \left\{\begin{array}{l}\mathbf{C}_3\mathrm{H}_7\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

This substitution has not yet been accomplished; but an analogous series of reactions has been effected with acetic acid.

By the action of sodium on acetic ether, one of the hydrogen atoms in the positive part of the compound becomes substituted by sodium, producing

$$\text{Monosodacetic ether}\ \ldots\ \ldots \left\{\begin{array}{l}\mathbf{C}\mathrm{H}_2\mathrm{Na}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. .$$

By acting on this body with the iodides of the C_nH_{2n+1} radicals, ethylic salts of the higher acids are produced.

On submitting monosodacetic ether to the action of ethylic iodide, for instance, butyric ether is produced—

$$\begin{array}{ccccccc}\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_2\mathrm{Na}\\ \mathbf{C}\mathrm{OEto}\end{array}\right. & + & \mathbf{C}_2\mathrm{H}_5\mathrm{I} & = & \left\{\begin{array}{l}\mathbf{C}(\mathrm{C}_2\mathrm{H}_5)\mathrm{H}_2\\ \mathbf{C}\mathrm{OEto}\end{array}\right. & + & \mathrm{NaI}.\\ \text{Monosodacetic ether.} & & \text{Ethylic iodide.} & & \text{Butyric ether.} & & \text{Sodic iodide.}\end{array}$$

FORMIC ACID.

$$\left\{\begin{array}{l}\mathrm{H}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. \text{ or } \mathbf{C}\mathrm{HOHo}.$$

Molecular weight =46. *Molecular volume* ☐☐. 1 *litre of formic acid vapour weighs* 23 *criths. Sp. gr. of liquid* 1·2353. *Fuses at* 1° C. *Boils at* 100° C.

Occurrence.—If red ants be made to pass over blue litmus-paper and be at the same time irritated, they leave a red streak behind them, produced by the formic acid which they eject. By placing the hand on an ant-hill, a tingling sensation is felt from the same cause, and the hand acquires the powerful and pleasant odour of formic acid.

Formic acid also occurs in the hairs of certain caterpillars and in the sting of nettles.

Formation.—1. Formic acid is produced in a very large number of chemical reactions, as in the oxidation of many organic bodies (such as starch, woody fibre, or tartaric acid) by a mixture of sulphuric acid and manganic oxide, or by potassic hydrate or chromic acid.

2. By the action of potassic hydrate on chloroform, potassic formate is generated:—

$$\underset{\text{Chloroform.}}{CHCl_3} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{4KHo} = \underset{\substack{\text{Potassic}\\\text{formate.}}}{CHOKo} + \underset{\substack{\text{Potassic}\\\text{chloride.}}}{3KCl} + \underset{\text{Water.}}{2OH_2}.$$

3. By the oxidation of methylic alcohol:—

$$\underset{\substack{\text{Methylic}\\\text{alcohol.}}}{\left\{\begin{matrix}H\\CH_2Ho\end{matrix}\right.} + O_2 = \underset{\substack{\text{Formic}\\\text{acid.}}}{\left\{\begin{matrix}H\\COHo\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

4. By heating equal weights of dry oxalic acid and glycerin together to 75° C., when the oxalic acid splits into formic acid and carbonic anhydride:—

$$\underset{\substack{\text{Oxalic}\\\text{acid.}}}{\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.} = \underset{\substack{\text{Formic}\\\text{acid.}}}{\left\{\begin{matrix}H\\COHo\end{matrix}\right.} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2}.$$

5. By digesting together at 100°, for forty-eight hours, potassic hydrate and carbonic oxide:—

$$\underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{CO} = \underset{\substack{\text{Potassic}\\\text{formate.}}}{\left\{\begin{matrix}H\\COKo\end{matrix}\right.}.$$

6. Formic acid is produced in small quantities by digesting carbon with permanganic acid.

Formic acid from any of these sources is obtained in the concentrated state by decomposing plumbic formate with sulphuretted hydrogen, and afterwards rectifying the acid over plumbic formate:—

$$\begin{array}{ccccccc} \begin{matrix}CHO\\CHO\end{matrix}Pbo'' & + & SH_2 & = & 2\left\{\begin{matrix}H\\COHo\end{matrix}\right. & + & PbS''. \\ \text{Plumbic formate.} & & \text{Sulphuretted hydrogen.} & & \text{Formic acid.} & & \text{Plumbic sulphide.} \end{array}$$

Character.—When heated with concentrated sulphuric acid, formic acid splits into water and carbonic oxide:—

$$\begin{array}{ccccc} \left\{\begin{matrix}H\\COHo\end{matrix}\right. & = & CO & + & OH_2. \\ \text{Formic acid.} & & \text{Carbonic oxide.} & & \text{Water.} \end{array}$$

Chlorine converts formic acid into hydrochloric acid and carbonic anhydride:—

$$\begin{array}{ccccccc} \left\{\begin{matrix}H\\COHo\end{matrix}\right. & + & Cl_2 & = & 2HCl & + & CO_2. \\ \text{Formic acid.} & & & & \text{Hydrochloric acid.} & & \text{Carbonic anhydride.} \end{array}$$

When heated with excess of mercuric oxide, it is converted into carbonic anhydride and water, the mercury being reduced to the metallic state:—

$$\begin{array}{ccccccccc} \left\{\begin{matrix}H\\COHo\end{matrix}\right. & + & HgO & = & CO_2 & + & Hg & + & OH_2. \\ \text{Formic acid.} & & \text{Mercuric oxide.} & & \text{Carbonic anhydride.} & & & & \text{Water.} \end{array}$$

ACETIC ACID.

$$\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right. .$$

Molecular weight =60. *Molecular volume* $\square\!\square$. 1 *litre of acetic acid vapour weighs* 30 *criths. Sp. gr. of liquid* 1·064. *Fuses at* +17°. *Boils at* 117°.

Occurrence.—Found in small quantities in the juices of plants and in animal fluids.

Manufacture.—1. By the destructive distillation of wood, a liquid is obtained which contains acetic acid; the acid is purified by being converted first into a calcic, and then into a sodic salt, the latter being afterwards decomposed by sulphuric acid.

2. By the oxidation of ethylic alcohol:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.} + O_2 = \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

Preparation.—Pure acetic acid may be obtained by distilling potassic diacetate:—

$$\underset{\text{Potassic diacetate.}}{\left\{\begin{array}{l}CH_3\\COKo\end{array}\right., \left\{\begin{array}{l}CH_3\\COHo\end{array}\right.} = \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}CH_3\\COKo\end{array}\right.} + \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.}.$$

Character.—Chlorine acts on acetic acid in sunlight, producing three chlorinated acids, in which chlorine is substituted for hydrogen:—

$$\underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.} + Cl_2 = \underset{\text{Monochloracetic acid.}}{\left\{\begin{array}{l}CH_2Cl\\COHo\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

$$\underset{\text{Monochloracetic acid.}}{\left\{\begin{array}{l}CH_2Cl\\COHo\end{array}\right.} + Cl_2 = \underset{\text{Dichloracetic acid.}}{\left\{\begin{array}{l}CHCl_2\\COHo\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

$$\underset{\text{Dichloracetic acid.}}{\left\{\begin{array}{l}CHCl_2\\COHo\end{array}\right.} + Cl_2 = \underset{\text{Trichloracetic acid.}}{\left\{\begin{array}{l}CCl_3\\COHo\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

The salts of acetic acid in which the hydrogen of the oxatyl is replaced by monad metals have the general formula

$$\left\{\begin{array}{l}CH_3\\COMo\end{array}\right..$$

The acetates of the dyad metals have the constitution represented by the following general formula :—

$$\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}O\text{-}O\\ \mathbf{C}O\text{-}O\\ \mathbf{C}H_3\end{array}\right. M'' \text{ or } \left\{\begin{array}{l}\mathbf{C}MeO\\ Mo''\\ \mathbf{C}MeO\end{array}\right. \text{ or } \begin{array}{l}\mathbf{C}MeO\text{-}O\\ \mathbf{C}MeO\text{-}O\end{array} M''.$$

By the action of phosphorous chloride, acetic acid yields acetylic chloride :—

$$\underset{\text{Acetic acid.}}{3\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Phosphorous chloride.}}{\mathbf{P}Cl_3} = \underset{\text{Acetylic chloride.}}{3\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OCl\end{array}\right.} + \underset{\text{Phosphorous acid.}}{\mathbf{P}OHHo_2}.$$

PROPIONIC ACID, *Methacetic Acid.*

$$\left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}OHo\end{array}\right. .$$

Molecular weight = 74. *Molecular volume* ☐☐. 1 *litre of propionic acid vapour weighs* 37 *criths. Boils at* 141°.

Preparation.—1. By the oxidation of metacetone—a liquid obtained by the distillation of a mixture of sugar and lime.

2. By the action of concentrated solution of potassic hydrate on sugar.

3. By the fermentation of glycerin, and also of sugar, by means of putrid cheese in the presence of calcic carbonate.

4. By the action of potassic hydrate or hydrochloric acid on abnormal ethylic cyanide (see p. 117).

5. By the action of carbonic anhydride on sodic ethide (see p. 118).

6. By the action of hydriodic acid on lactic acid :—

$$\underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathbf{C}MeHHo\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Hydriodic acid.}}{2HI} = \underset{\text{Propionic acid.}}{\left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2} + I_2.$$

BUTYRIC ACID, *Ethacetic Acid.*

$$\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{COHo}\end{array}\right..$$

Molecular weight =88. *Molecular volume* ☐☐. 1 *litre of butyric acid vapour weighs* 44 *criths. Sp. gr. of liquid* 0·9886. *Fuses below* −20°. *Boils at* 161° C.

Occurrence.—In butter, juice of flesh, perspiration, and many animal secretions.

Preparation.—1. By the fermentation of sugar with putrid cheese.

2. By the action of ethylic iodide on sodacetic ether (for reaction, see page 121).

VALERIC ACID, *Valerianic Acid.*

$$\left\{\begin{array}{l}\mathrm{CPrH_2}\\ \mathrm{COHo}\end{array}\right..$$

Molecular weight =102. *Molecular volume* ☐☐. 1 *litre of valeric acid vapour weighs* 51 *criths. Sp. gr. of liquid* 0·937. *Boils at* 175°.

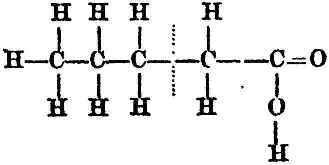
Occurrence.—In many plants, as in the roots of valerian and angelica.

Preparation.—By the oxidation of amylic alcohol with a mixture of sulphuric acid and dipotassic dichromate:—

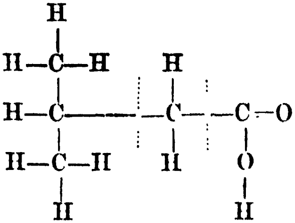
$$\underset{\text{Amylic alcohol.}}{\left\{\begin{array}{l}\mathrm{C(C_3H_7)H_2}\\ \mathrm{CH_2Ho}\end{array}\right.} + \mathrm{O_2} = \underset{\text{Valeric acid.}}{\left\{\begin{array}{l}\mathrm{C(C_3H_7)H_2}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Water.}}{\mathrm{OH_2}}.$$

Isomeric forms.—There are four possible isomers of valeric acid:—

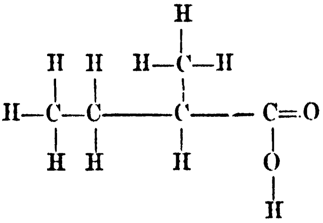
Normal valeric acid or propacetic acid ...... $\left\{\begin{array}{l}\mathrm{CPrH_2}\\ \mathrm{COHo}\end{array}\right.$ or $\left\{\begin{array}{l}\mathrm{CH_2(CH_2[CH_2(CH_3)])}\\ \mathrm{COHo}\end{array}\right..$



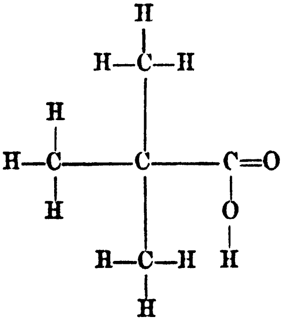
Isopropacetic acid ... $\left\{\begin{array}{l}\mathbf{C}\mathrm{Pr}\beta\mathrm{H}_2\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}\mathrm{H}_2[\mathbf{C}\mathrm{H}(\mathrm{CH}_3)_2].\\ \mathbf{C}\mathrm{OHo}.\end{array}\right.$



Methethacetic acid... $\left\{\begin{array}{l}\mathbf{C}\mathrm{EtMeH}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}\mathrm{H}(\mathrm{CH}_3)[\mathbf{C}\mathrm{H}_2(\mathrm{CH}_3)]\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$.



Trimethacetic acid ... $\left\{\begin{array}{l}\mathbf{C}\mathrm{Me}_3\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ or $\left\{\begin{array}{l}\mathbf{C}(\mathrm{CH}_3)_3\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$.



Of these, the normal, the isopropacetic, and the trimethacetic acid are known.

B. *SECONDARY FATTY ACIDS.*

General formula... $\left\{\begin{matrix}\mathrm{C(C_nH_{2n+1})_2H}\\ \mathrm{COHo}\end{matrix}\right.$.

Formation.—1. By the action of the iodides of the C_nH_{2n+1} radicals on disodacetic ether, the ethereal salts of these acids are produced.

2. By the action of a boiling solution of caustic potash upon the nitriles or abnormal cyanides of the secondary radicals.

DIMETHACETIC ACID, *or Isobutyric Acid.*

$$\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{COHo}\end{matrix}\right. .$$

Molecular weight =88. *Molecular volume* ☐☐. 1 *litre of dimethacetic acid vapour weighs* 44 *criths. Boils at* 152°. *Isomeric with butyric or ethacetic acid.*

Preparation.—1. As a potassic salt, by the action of methylic iodide on disodacetic ether and the subsequent decomposition, by alcoholic solution of potash, of the ethereal salt so formed :—

$$\begin{array}{ccccccc}\left\{\begin{matrix}\mathrm{CNa_2H}\\ \mathrm{COEto}\end{matrix}\right. & + & \mathrm{2MeI} & = & \left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{COEto}\end{matrix}\right. & + & \mathrm{2NaI.}\\ \text{Disodacetic ether.} & & \text{Methylic iodide.} & & \text{Dimethacetic ether.} & & \text{Sodic iodide.}\end{array}$$

$$\begin{array}{ccccccc}\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{COEto}\end{matrix}\right. & + & \mathrm{KHo} & = & \left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{COKo}\end{matrix}\right. & + & \mathrm{EtHo.}\\ \text{Dimethacetic ether.} & & \text{Potassic hydrate.} & & \text{Potassic dimethacetate.} & & \text{Alcohol.}\end{array}$$

2. By boiling isopropylic nitrile with solution of caustic potash :—

$$\begin{array}{ccccccccc}\left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{CN'''}\end{matrix}\right. & + & \mathrm{KHo} & + & \mathrm{OH_2} & = & \left\{\begin{matrix}\mathrm{CMe_2H}\\ \mathrm{COKo}\end{matrix}\right. & + & \mathrm{NH_3.}\\ \text{Isopropylic nitrile.} & & & & & & \text{Potassic dimethacetate.} & & \text{Ammonia.}\end{array}$$

Reaction.—By a hot solution of chromic acid dimethacetic acid is decomposed into carbonic anhydride and acetic acid:—

$$\underset{\text{Dimethacetic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{Me_2H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.} + 3\mathrm{O_2} = 2\mathbf{C}\mathrm{O_2} + 2\mathrm{OH_2} + \underset{\text{Acetic acid.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.}$$

Acetone is sometimes formed as an intermediate product.

Diethacetic acid, $\left\{\begin{matrix}\mathbf{C}\mathrm{Et_2H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.$, isomeric with caproic acid, and *diamylacetic acid*, $\left\{\begin{matrix}\mathbf{C}\mathrm{Ay_2H}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right.$, isomeric with lauric acid, have been prepared by the substitution of ethylic and amylic iodides in the above reaction.

C. *TERTIARY FATTY ACIDS.*

General formula .. $\left\{\begin{matrix}\mathbf{C}(\mathrm{C}_n\mathrm{H}_{2n+1})_3\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right..$

Formation.—As ethereal salts, by the action of the iodides of the $\mathrm{C}_n\mathrm{H}_{2n+1}$ radicals on trisodacetic ether.

TRIMETHACETIC ACID.

$$\left\{\begin{matrix}\mathbf{C}\mathrm{Me_3}\\ \mathbf{C}\mathrm{OHo}\end{matrix}\right..$$

Molecular weight** = 102. **Molecular volume** ☐☐. 1 **litre of trimethacetic acid vapour weighs** 51 **criths**. **Isomeric with valeric acid.

For the graphic formula of trimethacetic acid see p. 127.

Preparation.—As an ethereal salt, by the action of methylic iodide on trisodacetic ether:—

$$\underset{\text{Trisodacetic ether.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{Na_3}\\ \mathbf{C}\mathrm{OEto}\end{matrix}\right.} + \underset{\text{Methylic iodide.}}{3\mathrm{MeI}} = \underset{\text{Trimethacetic ether.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{Me_3}\\ \mathbf{C}\mathrm{OEto}\end{matrix}\right.} + \underset{\text{Sodic iodide.}}{3\mathrm{NaI}}.$$

CHAPTER XVII.

THE ACIDS.

2. *ACRYLIC OR OLEIC SERIES OF ACIDS.*

General formula of normal and secondary acids ... . $\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n})''(C_mH_{2m+1})\\ \mathbf{C}OHo\end{array}\right..$

This series is divided into normal, secondary, and olefine acids. In the normal acids $m=0$; in the secondary it must be a positive integer.

Most of the normal acids exist as ethereal salts of glycerin in natural fats and oils.

The following is a list of the acrylic series of acids:—

A. *NORMAL ACIDS.*

Acrylic acid	$\left\{\begin{array}{l}\mathbf{C}Me''H\\ \mathbf{C}OHo\end{array}\right.$	or	$\left\{\begin{array}{l}\mathbf{C}(CH_2)''H\\ \mathbf{C}OHo\end{array}\right..$
Crotonic acid................	$\left\{\begin{array}{l}\mathbf{C}Et''H\\ \mathbf{C}OHo\end{array}\right.$	or	$\left\{\begin{array}{l}\mathbf{C}(C_2H_4)''H\\ \mathbf{C}OHo\end{array}\right..$
Angelic acid	$\left\{\begin{array}{l}\mathbf{C}Pr''H\\ \mathbf{C}OHo\end{array}\right.$	or	$\left\{\begin{array}{l}\mathbf{C}(C_3H_6)''H\\ \mathbf{C}OHo.\end{array}\right..$
Pyroterebic acid	$\left\{\begin{array}{l}\mathbf{C}Bu''H\\ \mathbf{C}OHo\end{array}\right.$	or	$\left\{\begin{array}{l}\mathbf{C}(C_4H_8)''H\\ \mathbf{C}OHo\end{array}\right..$
Damaluric acid			$C_7H_{12}O_2$.
Damolic acid			$C_{13}H_{24}O_2$.
Moringic acid.......... . Cimicic acid	. ...		$C_{15}H_{28}O_2$.
Physetoleic acid......... Hypogæic acid .... Gaïdic acid..............	....		$C_{16}H_{30}O_2$.
Oleic acid			$\left\{\begin{array}{l}\mathbf{C}(C_{16}H_{32})''H\\ \mathbf{C}OHo\end{array}\right..$
Elaïdic acid.......................................			$C_{18}H_{34}O_2$.
Doeglic acid			$C_{19}H_{36}O_2$.
Brassic acid. (*Erucic acid*)	....		$C_{22}H_{42}O_2$.

B. *SECONDARY ACIDS.*

Methacrylic acid............ $\left\{\begin{matrix}\mathbf{C}\text{Me}''\text{Me}\\ \mathbf{C}\text{OHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(\text{CH}_2)''(\text{CH}_3)\\ \mathbf{C}\text{OHo}\end{matrix}\right.$.

Methylcrotonic acid ...... $\left\{\begin{matrix}\mathbf{C}\text{Et}''\text{Me}\\ \mathbf{C}\text{OHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(\text{C}_2\text{H}_4)''(\text{CH}_3)\\ \mathbf{C}\text{OHo}\end{matrix}\right.$.

Ethylcrotonic acid .... $\left\{\begin{matrix}\mathbf{C}\text{Et}''\text{Et}\\ \mathbf{C}\text{OHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(\text{C}_2\text{H}_4)''(\text{C}_2\text{H}_5)\\ \mathbf{C}\text{OHo}\end{matrix}\right.$.

C. *OLEFINE ACIDS.*

β Crotonic acid .. .... $\left\{\begin{matrix}\mathbf{C}\text{Me}''\text{H}\\ \mathbf{C}\text{H}_2\\ \mathbf{C}\text{OHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}(\text{CH}_2)''\text{H}\\ \mathbf{C}\text{H}_2\\ \mathbf{C}\text{OHo}\end{matrix}\right.$.

Formation of Normal Acids.—1. By the oxidation of the alcohols of the vinyl or $\text{C}_n\text{H}_{2n-1}\text{Ho}$ series:—

$$\underset{\text{Alcohol.}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''\text{H}\\ \mathbf{C}\text{H}_2\text{Ho}\end{matrix}\right.} + \text{O}_2 = \underset{\text{Acid}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''\text{H}\\ \mathbf{C}\text{OHo}\end{matrix}\right.} \quad \underset{\text{Water.}}{\text{OH}_2}.$$

2. By the oxidation of the aldehydes of the acrolein or $\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''\text{H}\\ \mathbf{C}\text{OH}\end{matrix}\right.$ series:—

$$\underset{\text{Aldehyde.}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''\text{H}\\ \mathbf{C}\text{OH}\end{matrix}\right.} + \text{O} = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''\text{H}\\ \mathbf{C}\text{OHo}\end{matrix}\right.}.$$

Formation of Secondary Acids.—By the action of phosphorous chloride, phosphoric chloride, phosphoric oxytrichloride or phosphoric anhydride upon the ethereal salts of secondary acids of the lactic series, the elements of water are removed and the ethereal salts of the acrylic secondary division of acids produced:—

$$3\underset{\substack{\text{Ethereal salt of}\\ \text{the lactic series.}}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n+1})_2\text{Ho}\\ \mathbf{C}\text{OEto}\end{matrix}\right.} + \underset{\substack{\text{Phosphorous}\\ \text{chloride.}}}{\mathbf{P}\text{Cl}_3} = 3\underset{\substack{\text{Ethereal salt of}\\ \text{the acrylic series.}}}{\left\{\begin{matrix}\mathbf{C}(\text{C}_n\text{H}_{2n})''(\text{C}_n\text{H}_{2n+1})\\ \mathbf{C}\text{OEto}\end{matrix}\right.}$$

$$+ \underset{\substack{\text{Phosphorous}\\ \text{acid.}}}{\mathbf{P}\text{OHHo}_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3\text{HCl}}.$$

Formation of Olefine Acids.—By the action of potassic hydrate upon the nitriles or abnormal cyanides of the C_nH_{2n-1} family of radicals:—

$$\underset{\text{Allylic nitrile.}}{\left\{\begin{matrix}CMe''H\\CH_2\\CN'''\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} + \underset{\text{Water.}}{OH_2} = \underset{\text{Potassic }\beta\text{ crotonate.}}{\left\{\begin{matrix}CMe''H\\CH_2\\COKo\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

Relations of the Acrylic to the Acetic Series of Acids.

The normal and secondary acids of the acrylic series, when treated with fused potassic hydrate, yield the potassic salts of two normal acids of the acetic series:—

$$\underset{\text{Acid of the acrylic series.}}{\left\{\begin{matrix}C(C_nH_{2n})''(C_mH_{2m+1})\\COHo\end{matrix}\right.} + \underset{\text{Potassic hydrate}}{2KHo} = \underset{\text{Potassic salt of acid of the acetic series.}}{\left\{\begin{matrix}C(C_mH_{2m+1})H_2\\COKo\end{matrix}\right.}$$

$$+ \underset{\text{Potassic salt of acid of the acetic series.}}{\left\{\begin{matrix}C(C_{n-2}H_{2n-3})H_2\\COKo\end{matrix}\right.} + H_2.$$

All the members of the acrylic series found in nature give acetic acid as one of the acids produced in this reaction. From this and other considerations, it is believed that their positive radicals all contain one atom of hydrogen and a dyad radical. They are normal acids; and by the action of fused potassic hydrate the dyad radical becomes substituted by two atoms of hydrogen. Thus:—

$$\underset{\text{Acrylic acid.}}{\left\{\begin{matrix}CMe''H\\COHo\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{matrix}H\\COKo\end{matrix}\right.} + H_2.$$

$$\underset{\text{Crotonic acid.}}{\left\{\begin{matrix}CEt''H\\COHo\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + H_2.$$

$$\underset{\text{Angelic acid.}}{\left\{\begin{matrix}CPr''H\\COHo\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} + \underset{\text{Potassic propionate.}}{\left\{\begin{matrix}CMeH_2\\COKo\end{matrix}\right.} + H_2.$$

Some of the secondary acids also give acetic acid when treated with fused potassic hydrate; but this can only happen when the dyad radical is ethylene, thus:—

$$\underset{\text{Methacrylic acid.}}{\left\{\begin{array}{l}\mathrm{CMe''Me}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic propionate.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic formate.}}{\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{COKo}\end{array}\right.} + \mathrm{H_2}.$$

$$\underset{\text{Methylcrotonic acid.}}{\left\{\begin{array}{l}\mathrm{CEt''Me}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic propionate.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COKo}\end{array}\right.} + \mathrm{H_2}.$$

$$\underset{\text{Ethylcrotonic acid.}}{\left\{\begin{array}{l}\mathrm{CEt''Et}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic butyrate.}}{\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COKo}\end{array}\right.} + \mathrm{H_2}.$$

ACRYLIC ACID.

$$\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right. .$$

Molecular weight $=72$. *Boils at about* 100°.

Preparation.—By the oxidation of acrolein with argentic oxide:—

$$\underset{\text{Acrolein.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COH}\end{array}\right.} + \underset{\text{Argentic oxide.}}{\mathrm{OAg_2}} = \underset{\text{Acrylic acid.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{Ag_2}.$$

Reactions.—1. Acrylic acid, under the influence of nascent hydrogen, produces propionic acid:—

$$\underset{\text{Acrylic acid.}}{\left\{\begin{array}{l}\mathrm{CMe''H}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{H_2} = \underset{\text{Propionic acid.}}{\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COHo}\end{array}\right.} .$$

2. Acrylic acid also combines directly with bromine, producing dibromopropionic acid.

OLEIC ACID.

$$\left\{\begin{array}{l}\mathbf{C}(C_{16}H_{32})''H\\ \mathbf{C}OHo.\end{array}\right.$$

Preparation.—Obtained in the purification of stearic acid.

Reaction.—Heated with potassic hydrate, it gives potassic acetate and palmitate :—

$$\underset{\text{Oleic acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_{16}H_{32})''H\\ \mathbf{C}OHo\end{array}\right.}+\underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo}=\underset{\substack{\text{Potassic}\\ \text{acetate.}}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OKo\end{array}\right.}+\underset{\text{Potassic palmitate.}}{\left\{\begin{array}{l}\mathbf{C}(C_{14}H_{29})H_2\\ \mathbf{C}OKo\end{array}\right.}+H_2.$$

CHAPTER XVIII.

THE ACIDS.

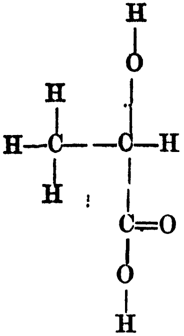
3. *LACTIC SERIES OF ACIDS.*

General formula of normal and secondary acids :—

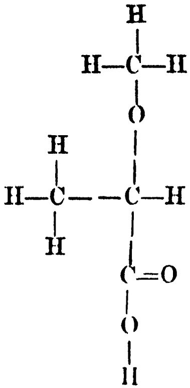
$$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OHo\end{array}\right..$$

In the normal acids m in this formula $=0$; but in the secondary acids it must be a positive integer.

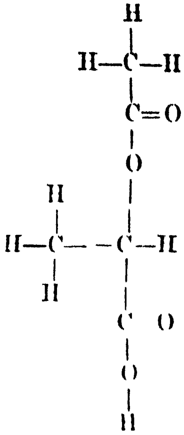
The members of the lactic series may be defined as acids containing one semimolecule of oxatyl, the fourth bond of the carbon of which is united with the carbon of a positive group containing one semimolecule of hydroxyl, or of the peroxide of a monad organic radical either positive or negative. The following examples will serve to illustrate this definition :—



Lactic acid



Methyl lactic acid



Aceto lactic acid

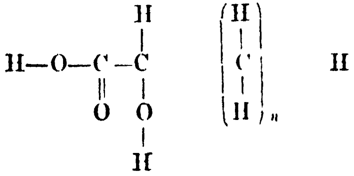
The acids of this series at present known, or which could be obtained by obvious processes, are classified into the following eight divisions :—

1. Normal Acids.
2. Etheric Normal Acids.
3. Secondary Acids.
4. Etheric Secondary Acids
5. Normal Olefine Acids.
6. Etheric Normal Olefine Acids.
7. Secondary Olefine Acids.
8. Etheric Secondary Olefine Acids

1st. *Normal Acids.*—A normal acid of the lactic series may be defined as one in which an atom of carbon is united with oxatyl, hydroxyl, and at least one atom of hydrogen. The general formula of these acids is therefore

$$\left\{\begin{array}{l}\mathbf{C}\overset{+}{\mathrm{R}}\mathrm{HHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right. .$$

In this formula $\overset{+}{R}$ may be either hydrogen or any monad positive organic radical. *The number of acids possessing the same atomic weight, and belonging to this division, is determined by the number of isomeric modifications of which the positive organic radical is susceptible.* Thus, of the acids containing two, three, or four atoms of carbon, there can be only one of each belonging to this division, because these acids cannot contain a positive organic radical higher in the series than ethyl, and this radical is not susceptible of isomeric modification; but a normal acid containing propyl can have one isomer in this division, the two acids containing respectively propyl ($\mathbf{C}EtH_2$) and isopropyl ($\mathbf{C}Me_2H$). For acids of this division containing normal positive organic radicals only, the following general graphic formula may be given:—

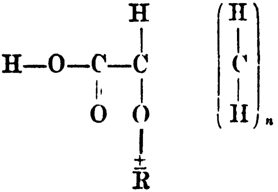


In the case of glycollic acid $n=0$.

The following are the acids at present known belonging to this division:—

Glycollic acid	$\left\{\begin{array}{l}\mathbf{C}H_2Ho \\ \mathbf{C}OHo\end{array}\right.$.
Lactic acid	$\left\{\begin{array}{l}\mathbf{C}MeHHo \\ \mathbf{C}OHo\end{array}\right.$.
Oxybutyric acid	$\left\{\begin{array}{l}\mathbf{C}EtHHo \\ \mathbf{C}OHo\end{array}\right.$.
Valerolactic acid...........	$\left\{\begin{array}{l}\mathbf{C}PrHHo \\ \mathbf{C}OHo\end{array}\right.$.
Leucic acid	$\left\{\begin{array}{l}\mathbf{C}BuHHo \\ \mathbf{C}OHo\end{array}\right.$.

2nd. *Etheric Normal Acids.*—An etheric normal acid of the lactic series is constituted like a normal acid, but contains a monad organic radical, positive or negative, in the place of the hydrogen of the *non-oxatylic* hydroxyl. The following is therefore the general formula of these acids: in the graphic formula *n*, as before, may $=0$.



$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{H{-}O{-}} & \mathrm{C} & \mathrm{{-}C} \\ & \| & | \\ & \mathrm{O} & \mathrm{O} \\ & & | \\ & & \overset{+}{\bar{\mathrm{R}}} \end{array} \left(\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C} \\ | \\ \mathrm{H} \end{array}\right)_n \mathrm{H} \quad \text{or} \quad \left\{\begin{array}{l} \mathrm{C}\overset{+}{\mathrm{R}}\mathrm{H}\overset{+}{\mathrm{R}}\mathrm{O} \\ \mathrm{COHo} \end{array}\right. .$$

The number of possible isomers belonging to this division is very great; for, in addition to those of which the normal acids containing $\overset{+}{\mathrm{R}}$ of the same value are susceptible, a host of others must result from the complementary variation of $\overset{+}{\mathrm{R}}$ and $\overset{+}{\mathrm{R}}$. The lowest member of the division, methylglycollic acid (isomeric with lactic acid), is the only one incapable of isomeric modification.

The following examples will serve to illustrate the constitution of the acids belonging to this division:—

Methylglycollic acid............ $\left\{\begin{array}{l}\mathrm{CH_2Meo} \\ \mathrm{COHo}\end{array}\right. .$

Ethyl-lactic acid .... $\left\{\begin{array}{l}\mathrm{CMeHEto} \\ \mathrm{COHo}\end{array}\right. .$

Aceto-lactic acid .... $\left\{\begin{array}{l}\mathrm{CMeHAco}^{*} \\ \mathrm{COHo}\end{array}\right. .$

3rd. *Secondary Acids.*—A secondary acid of the lactic series is one in which an atom of carbon is united with oxatyl, hydroxyl, and *two semimolecules* of a monad positive organic radical. The general formula of these acids is:—

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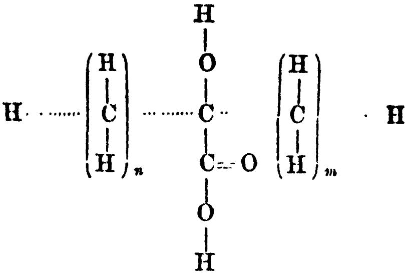
* Aco = peroxide of acetyl, $C_2H_3O_2$.



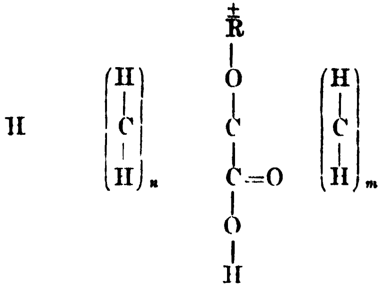
$$\mathrm{H}\cdots\cdots\left(\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right)_n\cdots\cdots\begin{array}{c}\mathrm{H}\\|\\\mathrm{O}\\|\\\mathrm{C}\\|\\\mathrm{C{=}O}\\|\\\mathrm{O}\\|\\\mathrm{H}\end{array}\cdots\left(\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right)_m\cdot\mathrm{H} \text{ or } \left\{\begin{array}{l}\mathbf{C}\overset{+}{\mathrm{R}}_2\mathrm{Ho}\\\mathbf{CO}\mathrm{Ho}\end{array}\right..$$

In the graphic expression, the values of *n* and *m* may differ; but both are positive integers, and neither may $=0$. In the symbolic formula $\overset{+}{\mathrm{R}}$ must be a monad positive organic radical. The following examples will serve to illustrate their constitution:—

Dimethoxalic acid	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Me_2Ho}\\\mathbf{CO}\mathrm{Ho}\end{array}\right..$
Ethomethoxalic acid	$\left\{\begin{array}{l}\mathbf{C}\mathrm{EtMeHo}\\\mathbf{CO}\mathrm{Ho}\end{array}\right..$
Diethoxalic acid	$\left\{\begin{array}{l}\mathbf{C}\mathrm{Et_2Ho}\\\mathbf{CO}\mathrm{Ho}\end{array}\right..$

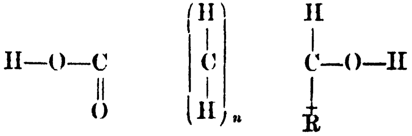
The number of acids possessing the same atomic weight, and belonging to this division, is determined, first, by the complementary variation of the two positive radicals, and, secondly, by the number of possible isomers of these radicals. The lowest two terms of the series are alone incapable of isomeric modification by either of the causes mentioned.

4th. *Etheric Secondary Acids.*—These acids stand in the same relation to the secondary as the etheric normal to the normal acids; they consequently contain a monad organic radical in the place of the hydrogen of the non-oxatylic hydroxyl. The following is therefore the general formula of these acids:—



$$\mathrm{H}\left\{\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right\}_n\begin{array}{l}\overset{+}{\mathrm{R}}\\|\\\mathrm{O}\\|\\\mathrm{C}\\|\\\mathrm{C}=\mathrm{O}\\|\\\mathrm{O}\\|\\\mathrm{H}\end{array}\left\{\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right\}_m\mathrm{H}\quad\text{or}\quad\left\{\begin{array}{l}\mathbf{C}\overset{+}{\mathrm{R}}_2\overset{+}{\mathrm{R}}\mathrm{o}\\\mathbf{C}\mathrm{OHo}\end{array}\right..$$

5th. *Normal Olefine Acids.*—A normal olefine acid belonging to the lactic series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is combined with not less than one atom of hydrogen. The following are the general graphic and symbolic formulæ of the acids belonging to this division:—



$$\begin{array}{c}\mathrm{H{-}O{-}C}\\\|\\\mathrm{O}\end{array}\left\{\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right\}_n\begin{array}{l}\mathrm{H}\\|\\\mathrm{C{-}O{-}H}\\|\\\overset{+}{\mathrm{R}}\end{array}\quad\text{or}\quad\left\{\begin{array}{l}\mathbf{C}\overset{+}{\mathrm{R}}\mathrm{HHo}\\(\mathrm{CH_2})_n\\\mathbf{C}\mathrm{OHo}\end{array}\right..$$

In both these formulæ n must be a positive integer and cannot $=0$, but $\overset{+}{\mathrm{R}}$ may be either hydrogen or a monad positive organic radical. The olefines of these acids may belong either to the ethylene or ethylidene series.

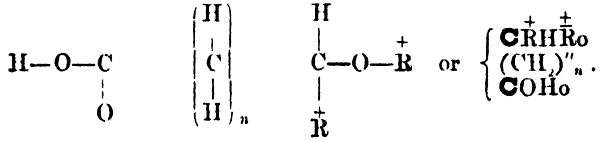
The following are the only acids at present known belonging to this division:—

Paralactic acid ... . $\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\\mathbf{C}\mathrm{H_2}\\\mathbf{C}\mathrm{OHo}\end{array}\right..$

Paraleucic acid .. .. $\left\{\begin{array}{l}\mathbf{C}\mathrm{H_2Ho}\\(\mathrm{C_4H_8})''\\\mathbf{C}\mathrm{OHo}\end{array}\right..$

The number of isomers in this division will obviously depend, first, upon the complementary variations of $\overset{+}{R}$ and $(CH_2)_n$; secondly, upon the isomeric modifications of which $\overset{+}{R}$ is susceptible; and thirdly, upon the isomeric modifications of $(CH_2)_n$.

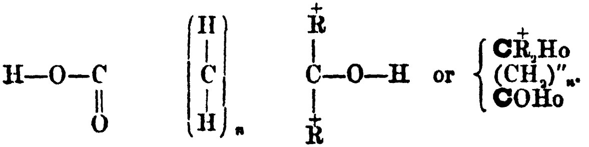
6th. *Etheric Normal Olefine Acids.*—These acids only differ from the normal olefine acids in having the hydrogen of the non-oxatylic hydroxyl replaced by an organic monad radical, positive or negative; their general formula is therefore,



$$\mathrm{H{-}O{-}\underset{\underset{\textstyle O}{\|}}{C}}\left(\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right)_n\underset{\underset{\textstyle \overset{+}{R}}{|}}{\overset{\overset{\textstyle H}{|}}{C}}{-}O{-}\overset{+}{R}\quad\text{or}\quad\left\{\begin{array}{l}\mathbf{C}\overset{+}{R}H\overset{\pm}{R}o\\(CH_2)''_n\\\mathbf{CO}Ho\end{array}\right..$$

As in the fifth division, n must be a positive integer and cannot $=0$, whilst $\overset{+}{R}$ may be either hydrogen or a monad positive organic radical; but $\overset{+}{R}$ must be a monad organic radical, either positive or negative

7th. *Secondary Olefine Acids*—A secondary olefine acid of this series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is also combined with two monad positive organic radicals, as shown in the following formulæ:—



$$\mathrm{H{-}O{-}\underset{\underset{\textstyle O}{\|}}{C}}\left(\begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\|\\\mathrm{H}\end{array}\right)_n\underset{\underset{\textstyle \overset{+}{R}}{|}}{\overset{\overset{\textstyle \overset{+}{R}}{|}}{C}}{-}O{-}H\quad\text{or}\quad\left\{\begin{array}{l}\mathbf{C}\overset{+}{R}_2Ho\\(CH_2)''_n\\\mathbf{CO}Ho\end{array}\right..$$

In both of these formulæ n must be a positive integer and cannot $=0$, and $\overset{+}{R}$ must be a monad positive radical.

8th. *Etheric Secondary Olefine Acids.*—These acids are related to the secondary olefine acids in the same way as the sixth division to the fifth. No member of the seventh or eighth division has yet been formed.

Formation of the Normal Acids.—1. By the oxidation of the glycols, or dihydric alcohols.

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{array}\right.} + O_2 = \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

2. By the oxidation of the $C_nH_{2n+1}Ho$ alcohols:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}H_2Ho\end{array}\right.} + O_2 = \underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

3. From the fatty acids, by converting them first into chlorosubstitution acids, and then acting upon these compounds with potassic hydrate:—

$$\underset{\text{Fatty acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})H_2\\ \mathbf{C}OHo\end{array}\right.} + Cl_2 = \underset{\text{Chlorofatty acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})HCl\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl:}$$

$$\underset{\text{Chlorofatty acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})HCl\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Normal acid of the lactic series.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})HHo\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Potassic chloride.}}{KCl.}$$

Formation of Secondary Acids.—By the action of the zinc compounds of the monad positive organic radicals upon ethylic oxalate, and the subsequent addition of water:—

$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{array}{l}\mathbf{C}OEto\\ \mathbf{C}OEto\end{array}\right.} + \underset{\text{Zinc compound of monad radical.}}{2\mathbf{Zn}(C_nH_{2n+1})_2} = \left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2(Zn''C_nH_{2n+1}O)\\ \mathbf{C}OEto\end{array}\right.$$

$$+ \quad \mathbf{Zn}(C_nH_{2n+1})Eto;$$

$$\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2(Zn''C_nH_{2n+1}O)\\ \mathbf{C}OEto\end{array}\right. + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Secondary acid.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})_2Ho\\ \mathbf{C}OEto\end{array}\right.}$$

$$+ \underset{\text{Hydride of radical.}}{\left\{\begin{array}{l}C_nH_{2n+1}\\ H\end{array}\right.} + \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2.}$$

***Formation of Olefine Acids.*—By uniting a dyad positive organic radical with carbonic oxydichloride (*phosgene gas*) under**

the influence of sunlight, and subsequently acting upon the product with potassic hydrate:—

$$\underset{\text{Ethylene.}}{''\left\{\begin{array}{l}\mathbf{C}H_2\\ \mathbf{C}H_2\end{array}\right.} + \underset{\substack{\text{Carbonic oxydi-}\\ \text{chloride}\\ \text{(Phosgene gas.)}}}{\mathbf{C}OCl_2} = \underset{\substack{\beta\text{ Chlorpropionylic}\\ \text{chloride.}}}{\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ \mathbf{C}H_2(COCl)\end{array}\right.};$$

$$\underset{\substack{\beta\text{ Chlorpropionylic}\\ \text{chloride.}}}{\left\{\begin{array}{l}\mathbf{C}H_2Cl\\ \mathbf{C}H_2(COCl)\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{3KHo} = \underset{\substack{\text{Potassic}\\ \text{paralactate.}}}{\left\{\begin{array}{l}\mathbf{C}H_2Ho\\ \mathbf{C}H_2(COKo)\end{array}\right.} + \underset{\substack{\text{Potassic}\\ \text{chloride.}}}{2KCl} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Relations of the Lactic to the Acetic Series of Acids.

1. The transformation of the acetic or fatty into the normal lactic series of acids has been mentioned above (p. 141).

2. The converse operation is effected with the normal and secondary acids of the lactic series by means of hydriodic acid:—

$$\underset{\text{Acid of lactic series}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OHo\end{array}\right.} + \underset{\substack{\text{Hydriodic}\\ \text{acid.}}}{2HI} = \underset{\text{Acid of acetic series.}}{\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})H\\ \mathbf{C}OHo\end{array}\right.}$$

$$+ \underset{\text{Water.}}{\mathbf{O}H_2} + I_2.$$

If m does not $=0$, the fatty acid will be a secondary one, like the member of the lactic series from which it is derived.

Relations of the Lactic to the Acrylic Series of Acids.

If the ethereal salts of the secondary acids of the lactic series be treated with phosphorous chloride, phosphoric chloride, phosphoric oxychloride, or phosphoric anhydride, the ethereal salts of the secondary acids of the acrylic series are produced:—

$$\underset{\text{Ethereal salt of lactic series.}}{3\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m+1})Ho\\ \mathbf{C}OEto\end{array}\right.} + \underset{\substack{\text{Phosphorous}\\ \text{chloride.}}}{\mathbf{P}Cl_3} = \underset{\text{Ethereal salt of acrylic series.}}{3\left\{\begin{array}{l}\mathbf{C}(C_nH_{2n+1})(C_mH_{2m})''\\ \mathbf{C}OEot\end{array}\right.}$$

$$+ \underset{\substack{\text{Phosphorous}\\ \text{acid.}}}{\mathbf{P}OHHo_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3HCl}.$$

This reaction has not yet been accomplished with the normal acids of the lactic series.

A secondary lactic acid *minus* OH_2 = an acrylic acid. The reverse of this operation has not been performed.

LACTIC ACID.

$$\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}OHo\end{matrix}\right. .$$

Sp. gr. of liquid 1·215.

Occurrence.—In sour milk, *Sauerkraut*, fluids of muscular tissue, gastric juice, saliva of diabetic patients. In the acid liquor of starch-factories, in blood, urine, tears, bile, &c. It is also a general product of putrefactive fermentation. The acid contained in animal fluids is *paralactic acid* (see p. 145).

Preparation.—By fermenting sugar with putrid cheese.

For other processes, see pages 147 and 148.

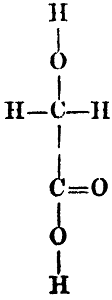
Its salts have the following general formulæ:—

$$\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}OMo\end{matrix}\right. . \qquad \begin{matrix}\left\{\begin{matrix}\mathbf{C}MeHHo\\ \mathbf{C}O\text{-}O\end{matrix}\right.\\ \left\{\begin{matrix}\mathbf{C}O\text{-}O\\ \mathbf{C}MeHHo\end{matrix}\right.\end{matrix}M''.$$

Salts of monad metals. Salts of dyad metals.

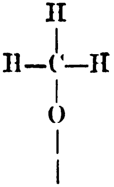
Isomerism in the Lactic Series.

The synthetical study of the acids of this series affords an insight into numerous and interesting cases of isomerism. Commencing with the lowest member of the series, we have for glycollic acid the formula



$$\begin{array}{c}H\\ |\\ O\\ |\\ H-C-H\\ |\\ C=O\\ |\\ O\\ |\\ H\end{array}$$

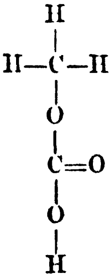
An inspection of this formula shows that glycollic acid admits of no isomeric modification, except with a total change of type. The part of the formula below the dotted line represents oxatyl, which cannot be altered without sacrificing the acid character of the compound; there remains therefore only the part of the formula above the dotted line, which admits of the following modification:—



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{O} \\ | \\ | \end{array}$$

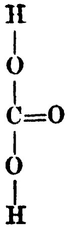
The acid represented by the formula so modified no longer comes within the definition of the lactic series. It is carbomethylic acid, and differs essentially from glycollic acid and the lactic series in general, inasmuch as the carbon of its negative radical, oxatyl, is linked to the carbon of the positive radical by oxygen*.

* Bearing this constitution of carbomethylic acid in mind, we have only to go one step further in order to perceive the constitution of carbonic acid itself, and the explanation of the anomalous basicity of this acid; for if, in the above graphic formula for carbomethylic acid, we replace the methyl by hydrogen, we have:—



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{O} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H} \end{array}$$

Carbomethylic acid.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{O} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H} \end{array}$$

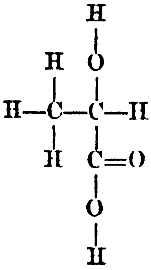
Carbonic acid.

It is thus evident that the radical oxatyl, when united with hydroxyl, has sufficient negative power to produce a feebly dibasic acid; but inasmuch as

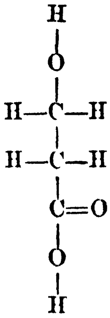
There being no decisive evidence that *homolactic acid* differs from glycollic acid, experiment and theory both agree in asserting that the formula $C_2H_4O_3$ represents only one acid in the lactic series.

Proceeding now one step higher in this series, we have in the formula of lactic acid an expression capable of the following three variations without quitting the lactic type:—

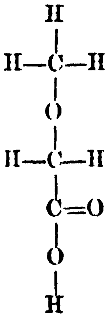
No. 1.



No. 2.



No. 3.



Or, expressed symbolically:—

No. 1.

$$\begin{cases}\text{CMeHHo}\\ \text{COHo}\end{cases}.$$

No. 2.

$$\begin{cases}\text{CH}_2\text{Ho}\\ \text{CH}_2(\text{COHo})\end{cases}\text{ or }\begin{cases}\text{CH}_2\text{Ho}\\ \text{CH}_2\\ \text{COHo}\end{cases}.$$

No. 3.

$$\begin{cases}\text{CH}_2\text{Meo}\\ \text{COHo}\end{cases}.$$

All the acids represented by the above formulæ are known. The first expresses the constitution of lactic acid, which belongs to the normal division $\left(\begin{cases}\text{C}\overset{+}{\text{R}}\text{HHo}\\ \text{COHo}\end{cases}\right)$ of the series, described at page 135; the second shows the atomic arrangement of paralactic acid; whilst the third represents methylglycollic acid. The proof that the first two of these acids are so constituted is afforded by the synthetic processes sometimes

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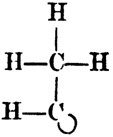
carbonic acid is not included in the category of organic acids, it forms no exception to the law that an organic acid containing *n* semimolecules of oxatyl is *n*-basic.

employed to produce them; for ethylidenic cyanhydrate is converted by ebullition with potash into a salt of lactic acid, whilst ethylenic cyanhydrate is transformed under similar circumstances into paralactic acid. It has also been mentioned above, that paralactic acid is produced by the action of phosgene gas upon ethylene. Now the formation of ethylidene, or rather of its compounds, scarcely leaves a doubt that this body, if isolated, would have the following atomic constitution:—

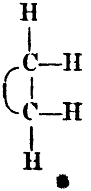


$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C\circlearrowright \end{array} \quad \text{or} \quad \left\{\begin{array}{l} CH_3 \\ ''CH \end{array}\right. :$$

it would consist of a semimolecule of methyl and an atom of hydrogen, both united with an atom of carbon two of the bonds of which satisfy each other. Thus the formation of ethylidene chloride from aldehyde and phosphoric chloride takes place as follows:—

$$\underset{\text{Aldehyde}}{\left\{\begin{array}{l} CH_3 \\ CHO \end{array}\right.} + \underset{\text{Phosphoric chloride}}{PCl_5} = \underset{\text{Ethylidenic chloride}}{\left\{\begin{array}{l} CH_3 \\ CHCl_2 \end{array}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{POCl_3},$$

the oxygen in the aldehyde being simply replaced by chlorine. There now only remains one possible formula for ethylene, viz.



$$\begin{array}{c} H \\ | \\ C-H \\ | \\ C-H \\ | \\ H \end{array} \quad \text{or} \quad ''\left\{\begin{array}{l} CH_2 \\ CH_2 \end{array}\right. .$$

Such, then, being the constitution of ethylidene and ethylene, it follows that the former ought to give rise to an acid of the constitution shown in formula No. 1, whilst ethylene should produce an acid agreeing with formula No. 2. The acids actually produced from these sources are lactic and paralactic acids; hence No. 1 is the constitutional formula of lactic acid, and No. 2 that of paralactic acid—a conclusion which harmonizes perfectly with all the reactions in which the production of these acids can be traced. Thus in the formation of lactic acid by the oxidation of propylic glycol, we have

$$\underset{\text{Propylic glycol.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{H_2Ho}\end{array}\right.} + \mathrm{O}_2 = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

Again, in the production of this acid from ethylidenic cyanhydrate,

$$\underset{\text{Ethylidenic cyanhydrate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(CN''')}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} = \underset{\text{Potassic lactate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(COKo)}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H}_3}.$$

The formula given for potassic lactate in this equation is only apparently different in type from that previously used for lactic acid, since

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{HHo(COKo)}\end{array}\right. = \mathbf{C}\mathrm{MeHHo(COKo)} = \left\{\begin{array}{l}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OKo}\end{array}\right..$$

In the reaction by which chloropropionic acid is transformed into lactic acid we have the following change:—

$$\underset{\text{Chloropropionic acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeHCl}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic lactate.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Potassic chloride.}}{\mathrm{KCl}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

The production of lactamic acid (*alanin*), and that of lactic acid from the latter by the action of nitrous acid, are also clearly confirmatory of the above view.

$$\underset{\text{Ammonic aldehyde.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{O(N^{v}H_4)}\end{array}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathbf{N}\mathrm{CH}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Lactamic acid. (alanin).}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeH(N'''H_2)}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Ammonic chloride.}}{\mathbf{N}\mathrm{H_4Cl}}:$$

$$\underset{\text{Lactamic acid (alanin).}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeH(N'''H_2)}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Nitrous acid.}}{\mathbf{N}\mathrm{OHo}} = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{MeHHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} + \mathrm{N}_2.$$

Not the least interesting reaction illustrative of the constitution of lactic acid is the formation of this acid by the action of nascent hydrogen upon pyruvic acid:—

$$\underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{COHo}\end{array}\right.} + \mathrm{H}_2 = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{COHo}\end{array}\right.}.$$

In a similar manner it can be demonstrated that the above formula No. 2 expresses the constitution of paralactic acid, which belongs to the fifth or olefine division of these acids,

$$\left\{\begin{array}{l}\mathrm{C\overset{+}{R}HHo}\\ (\mathrm{CH}_2)''_n(\mathrm{COHo})\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathrm{C\overset{+}{R}HHo}\\ (\mathrm{CH}_2)''_n\\ \mathrm{COHo}\end{array}\right..$$

That paralactic acid possesses this constitution is proved, first, by its production from cyanhydric glycol—

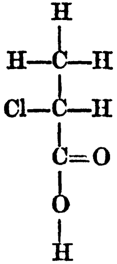
$$\underset{\text{Cyanhydric glycol.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2(CN''')}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} + \underset{\text{Water.}}{\mathrm{OH}_2} = \underset{\text{Potassic paralactate.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH}_2\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Ammonia.}}{\mathrm{NH}_3};$$

secondly, by its formation from phosgene gas and ethylene (see p. 142); and thirdly, by its conversion into malonic acid by the oxidizing action of dipotassic dichromate:—

$$\underset{\text{Paralactic acid.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH}_2\\ \mathrm{COHo}\end{array}\right.} + \mathrm{O}_2 = \underset{\text{Malonic acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH}_2\\ \mathrm{COHo}\end{array}\right.} + \mathrm{OH}_2.$$

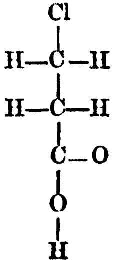
By the action of water upon the chloride of β chlorpropionyl, a body of the composition of chloropropionic acid is obtained; but inasmuch as this body yields paralactic acid by ebullition with potash, whilst chloropropionic acid gives under the same circumstances lactic acid, it follows that the former chloro-acid must be isomeric, and not identical, with the latter. Now, although the formula of propionic acid does not admit of any isomer, yet that of chloropropionic acid does, as is seen in the following graphic formulæ:—

No. 1.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{Cl{-}C{-}H} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H} \end{array}$$

No. 2.



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{C{-}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H} \end{array}$$

A comparison of these formulæ with those of lactic and paralactic acids (p. 145) shows at a glance that No. 1 is the chloropropionic acid which yields lactic acid, whilst No. 2 is iso-chloropropionic acid, which, by the substitution of its chlorine by hydroxyl, must yield paralactic acid. By the action of nascent hydrogen, both isomeric chlorides will obviously produce the same propionic acid.

The cause of the isomerism of methyl-glycollic acid (No. 3, p. 145) is so obvious as to require no further explanation. Proceeding to the next higher stage in the series, such is the rapid increase of isomeric forms, that we now encounter no less than eight possible isomers, all within the lactic family.

Normal. No. 1. $\left\{\begin{array}{l}\mathrm{CEtHHo}\\ \mathrm{COHo}\end{array}\right. .$

Secondary. No. 2. $\left\{\begin{array}{l}\mathrm{CMe_2Ho}\\ \mathrm{COHo}\end{array}\right. .$

Etheric normal

No. 3. $\left\{\begin{array}{l}\mathrm{CH_2Eto}\\ \mathrm{COHo}\end{array}\right. .$

No. 4. $\left\{\begin{array}{l}\mathrm{CMeHMeo}\\ \mathrm{COHo}\end{array}\right. .$

Normal olefine.

No. 5. $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. .$

No. 6. $\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right. .$

No. 7. $\left\{\begin{array}{l}\mathrm{CMeHHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. .$

Etheric normal olefine.

No. 8. $\left\{\begin{array}{l}\mathrm{CH_2Meo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. .$

Of these acids, Nos. 1, 2, and 3 are known. No. 1 is oxybutyric acid; No. 2 is dimethoxalic acid, which is identical with acetonic acid. This being the case, the formation of the latter by the action of hydrocyanic and hydrochloric acids upon acetone is easily intelligible:—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COMe}\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathrm{NCH}} + \underset{\text{Water.}}{2\mathrm{OH_2}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Acetonic or dimethoxalic acid.}}{\left\{\begin{matrix}\mathrm{CMe_2Ho}\\ \mathrm{COHo}\end{matrix}\right.} + \mathrm{NH_4Cl.}$$

The third of the above formulæ is that of ethyl-glycollic acid.

Of the possible acids containing five atoms of carbon, only two, viz. ethomethoxalic acid and valerolactic acid, are known. The cause of the isomerism of these two acids is seen at once from an inspection of their constitutional formulæ:—

Ethomethoxalic acid ...... $\left\{\begin{matrix}\mathrm{CEtMeHo}\\ \mathrm{COHo}\end{matrix}\right.$.

Valerolactic acid...... . $\left\{\begin{matrix}\mathrm{CPrHHo}\\ \mathrm{COHo}\end{matrix}\right.$.

Of acids containing six atoms of carbon, the following three are known:—

Leucic acid .. .. $\left\{\begin{matrix}\mathrm{CBuHHo}\\ \mathrm{COHo}\end{matrix}\right.$.

Diethoxalic acid .... $\left\{\begin{matrix}\mathrm{CEt_2Ho}\\ \mathrm{COHo}\end{matrix}\right.$.

Paraleucic acid .. .. $\left\{\begin{matrix}\mathrm{CH_2Ho}\\ (\mathrm{C_4H_8})''\\ \mathrm{COHo}\end{matrix}\right.$.

The above formula for leucic acid is founded upon a reaction for the synthetical production of amidocaproic acid from valeric aldehyde and hydrocyanic acid. Valeric acid contains butyl; consequently valeric aldehyde has the constitution expressed by the formula $\left\{\begin{matrix}\mathrm{Bu}\\ \mathrm{COH}\end{matrix}\right.$; and the reaction in question is therefore explained by the following equation:—

$$\underset{\text{Ammonic valeric aldehyde.}}{\left\{\begin{matrix}\mathrm{Bu}\\ \mathrm{CO(N^vH_4)}\end{matrix}\right.} + \underset{\text{Hydrocyanic acid.}}{\mathrm{NCH}} + \underset{\text{Water.}}{\mathrm{OH_2}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} = \underset{\text{Amidocaproic acid (leucin).}}{\left\{\begin{matrix}\mathrm{CBuH(N''H_2)}\\ \mathrm{COHo}\end{matrix}\right.} + \underset{\text{Ammonic chloride.}}{\mathrm{NH_4Cl.}}$$

Such being the rational formula of amidocaproic acid, its transformation into leucic acid by nitrous acid determines the constitution of leucic acid:—

$$\underset{\text{Amidocaproic acid.}}{\left\{\begin{array}{l}CBuH(N'''H_2)\\COHo\end{array}\right.} + \underset{\text{Nitrous acid.}}{NOHo} = \underset{\text{Leucic acid.}}{\left\{\begin{array}{l}CBuHHo\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2} + N_2.$$

CHAPTER XIX.

THE ACIDS

4. *PYRUVIC SERIES.*

General formula...... $\left\{\begin{array}{l}CO(C_nH_{2n+1})\\COHo\end{array}\right.$.

In this formula n may $=0$.

The following list contains all the known members of this series:—

Pyruvic acid	$\left\{\begin{array}{l}COMe\\COHo\end{array}\right.$.	Boils at 165°.
Convolvulinoleic acid...	$\left\{\begin{array}{l}CO(C_{11}H_{23})\\COHo\end{array}\right.$.	Fuses at 42°.
Jalapinoleic acid...... .	$\left\{\begin{array}{l}CO(C_{14}H_{29})\\COHo\end{array}\right.$.	,, 65°.
Ricinoleic acid	$\left\{\begin{array}{l}CO(C_{16}H_{33})\\COHo\end{array}\right.$.	,, 0°.

Pyruvic acid only is well known.

The first member of this series would have the formula $\left\{\begin{array}{l}COH\\COHo\end{array}\right.$. This acid is believed to be formed by the dehydration of glyoxylic acid; but its existence has not yet been satisfactorily demonstrated:—

$$\underset{\text{Glyoxylic acid.}}{\left\{\begin{array}{l}CHHo_2\\COHo\end{array}\right.} - OH_2 = \underset{\text{Glyoxalic acid.}}{\left\{\begin{array}{l}COH\\COHo\end{array}\right.}.$$

The aldehyde of this acid, however, is known. It is called glyoxal, and its formula is:—

$$\left\{\begin{array}{l}COH\\COH\end{array}\right..$$

Glyoxal is produced by the oxidation of ethylic alcohol by nitric acid:—

$$\underset{\text{Ethylic alcohol.}}{\left\{\begin{array}{l}CH_3\\CH_2Ho\end{array}\right.} + O_3 = \underset{\text{Glyoxal.}}{\left\{\begin{array}{l}COH\\COH\end{array}\right.} + \underset{\text{Water.}}{2OH_2}.$$

These acids are the semi-ketones of oxalic acid, and they stand in much the same relation to this acid as that which acetone occupies with regard to acetic acid:—

$$\underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.} : \quad \underset{\text{Acetone.}}{\left\{\begin{array}{l}CH_3\\COMe\end{array}\right.}.$$

$$\underset{\text{Oxalic acid.}}{\left\{\begin{array}{l}COHo\\COHo\end{array}\right.} : \quad \underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}COMe\\COHo\end{array}\right.}.$$

The pyruvic series is also closely related to the lactic series; pyruvic acid absorbs hydrogen and is converted into normal lactic acid:—

$$\underset{\text{Pyruvic acid.}}{\left\{\begin{array}{l}COMe\\COHo\end{array}\right.} + H_2 = \underset{\text{Lactic acid.}}{\left\{\begin{array}{l}CMeHHo\\COHo\end{array}\right.}.$$

5. *THE GLYOXYLIC SERIES OF ACIDS.*

General formula... $\left\{\begin{array}{l}C(C_nH_{2n+1})Ho_2\\COHo\end{array}\right.$ or $\left\{\begin{array}{l}C_nH_{2n}Ho\\C_mH_{2m-1}Ho.\\COHo\end{array}\right.$

In the second formula n may $=0$.

The two following acids of this series are known:—

	Formula.	Physical condition.
Glyoxylic acid ...	$\left\{\begin{array}{l}CHHo_2\\COHo\end{array}\right..$	Syrupy, crystalline hydrate.
Glyceric acid	$\left\{\begin{array}{l}CH_2Ho\\CHHo.\\COHo\end{array}\right.$	Syrupy.

These acids are trihydric, but monobasic, and are related to the glycerin series of alcohols in the same way that the members of the lactic series are related to the glycols:—

$$\underset{\text{Glycol.}}{\left\{\begin{array}{l}CH_2Ho\\CH_2Ho\end{array}\right.}\cdot\qquad\qquad\underset{\text{Glycollic acid.}}{\left\{\begin{array}{l}CH_2Ho\\COHo\end{array}\right.}\cdot$$

$$\underset{\text{Glycerin.}}{\left\{\begin{array}{l}CH_2Ho\\CHHo\\CH_2Ho\end{array}\right.}.\qquad\qquad\underset{\text{Glyceric acid.}}{\left\{\begin{array}{l}CH_2Ho\\CHHo\\COHo\end{array}\right.}.$$

By a reaction similar to that which is believed to produce glyoxalic acid from glyoxylic acid, glyceric acid yields pyruvic acid:—

$$\underset{\text{Glyceric acid.}}{\left\{\begin{array}{l}CH_2Ho\\CHHo\\COHo\end{array}\right.}\;-\;OH_2\;=\;\underset{\text{Pyruvic acid}}{\left\{\begin{array}{l}CH_3\\CO\\COHo\end{array}\right.}.$$

CHAPTER XX.

THE ACIDS.

6. *THE BENZOIC OR AROMATIC SERIES OF ACIDS.*

$$\text{General formula}\ldots\left\{\begin{array}{l}C_nH_{2n-7}\\COHo\end{array}\right..$$

Formation.—1. By the oxidation of the aromatic or $C_nH_{2n-7}Ho$ alcohols:—

$$\underset{\text{Benzylic alcohol.}}{\left\{\begin{array}{l}C_6H_5\\CH_2Ho\end{array}\right.}\;+\;O_2\;=\;\underset{\text{Benzoic acid.}}{\left\{\begin{array}{l}C_6H_5\\COHo\end{array}\right.}\;+\;OH_2.$$

2. By the oxidation of the aromatic aldehydes. Thus benzoic acid is formed from benzoic aldehyde, or oil of bitter almonds (see p. 112).

3. By the action of alkalies on the nitriles or abnormal cyanides. Thus potassic benzoate is formed by the action of potash upon Benzonitrile:—

$$\left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CN'''}\end{matrix}\right. + \mathrm{KHo} + \mathrm{OH_2} = \left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{COKo}\end{matrix}\right. + \mathrm{NH_3}.$$

Benzonitrile. Potassic benzoate. Ammonia.

4. By the action of sodium and carbonic anhydride on the bromides of the C_nH_{2n-7} radicals:—

$$\mathrm{C_6H_5Br} + \mathrm{Na_2} + \mathrm{CO_2} = \left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CONao}\end{matrix}\right. + \mathrm{NaBr}.$$

Phenylic bromide or monobrombenzol. Sodic benzoate.

5. Some members of the series are produced by the oxidation of the hydrides of the C_nH_{2n-7} radicals:—

$$\mathrm{C_6Me_2H_4} + \mathrm{O_3} = \left\{\begin{matrix}\mathrm{C_6MeH_4}\\ \mathrm{COHo}\end{matrix}\right. + \mathrm{OH_2}.$$

Dimethyl-benzol. Toluylic acid.

6. The acids of the aromatic series may be obtained from the monamines of the series containing one atom less of carbon.

Thus Phenylamine, when distilled with oxalic acid, produces phenylformamide:—

$$\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right. + \mathrm{NH_2(C_6H_5)} = \mathrm{NH(C_6H_5)(CHO)} + \mathrm{OH_2} + \mathrm{CO_2}$$

Oxalic acid. Phenylamine. Phenylformamide. Water. Carbonic anhydride.

Phenylformamide, by the action of heat, gives water and benzonitrile:—

$$\mathrm{NH(C_6H_5)(CHO)} = \mathrm{OH_2} + \left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CN'''}\end{matrix}\right..$$

Phenylformamide. Benzonitrile.

Benzonitrile, heated with potassic hydrate, gives potassic benzoate and ammonia:—

$$\left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CN'''}\end{matrix}\right. + \mathrm{KHo} + \mathrm{OH_2} = \left\{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{COKo}\end{matrix}\right. + \mathrm{NH_3}.$$

Benzonitrile. Potassic hydrate. Potassic benzoate. Ammonia.

Toluylic acid, $\left\{\begin{matrix}\mathrm{C_6H_4Me}\\ \mathrm{COHo}\end{matrix}\right.$, can thus be obtained from toluidine, $\mathrm{NH_2(C_6H_4Me)}$.

The following terms of this series are known :—

		Melting-point.	Boiling-point.
Phenoic acid ……	$\left\{\begin{array}{l}\mathbf{C}_5H_3\\ \mathbf{C}OHo\end{array}\right.$	……… 60°.	——
Collinic acid ……		……… 97°.	——
Benzenic acid ……		above…110°.	235°.
Benzoic acid …………	$\left\{\begin{array}{l}\mathbf{C}_6H_5\\ \mathbf{C}OHo\end{array}\right.$ …………	121°·4.	239°.
Toluylic acid …………	$\left\{\begin{array}{l}\mathbf{C}_6MeH_4\\ \mathbf{C}OHo\end{array}\right.$ ………	175°·0.	——
Alpha-toluylic acid ……	$\left\{\begin{array}{l}\mathbf{C}PhH_2\\ \mathbf{C}OHo\end{array}\right.$ …………	76°·5.	265°·5.
Xylic acid ……………	$\left\{\begin{array}{l}\mathbf{C}_6Me_2H_3\\ \mathbf{C}OHo\end{array}\right.$ ………	103°·0.	273°.
		126°·0.	——
		163°·0.	——
Alpha-xylic acid ………	$\left\{\begin{array}{l}\mathbf{C}(C_6MeH_4)H_2\\ \mathbf{C}OHo\end{array}\right.$ …	42°·0.	——
Cuminic acid ……..	$\left\{\begin{array}{l}\mathbf{C}_9H_{11}\\ \mathbf{C}OHo\end{array}\right.$ ……… ..	92°·0.	——
Alpha-cymic acid ……	$\left\{\begin{array}{l}\mathbf{C}_6Et_2H_3\\ \mathbf{C}OHo\end{array}\right.$ ………	——	——

These acids have the same constitution as those of the acetic series, but contain the C_nH_{2n-7} radicals.

They have been much less studied than the acetic series; and further investigation will probably bring to light other series holding towards them the same relation as the acrylic, glycollic, pyruvic, and glyoxylic series bear to the acetic series. Already an acryloid acid of this section is known corresponding to alpha-xylic acid :—

$$\left\{\begin{array}{l}\mathbf{C}(C_7H_7)H_2\\ \mathbf{C}OHo\end{array}\right. . \qquad \left\{\begin{array}{l}\mathbf{C}(C_7H_6)''H\\ \mathbf{C}OHo\end{array}\right. .$$

Alpha-xylic acid. Cinnamic acid.

Cinnamic acid is decomposed, like the acids of the acrylic series, when heated with fused potassic hydrate; it gives, under these circumstances, potassic acetate and benzoate. For the analogous reaction in the acrylic series see p. 132.

Atropic acid, obtained by the action of alkalies on atropine, has the formula $\left\{\begin{array}{l}C_8H_7\\COHo\end{array}\right.$, and is isomeric with cinnamic acid.

Salicylic acid (with which oxybenzoic acid and parabenzoic acid are isomeric) is the lactic acid of benzoic acid:—

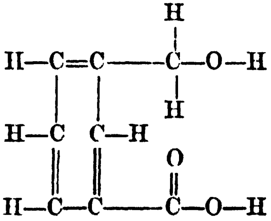
$$\underset{\text{Benzoic acid.}}{\left\{\begin{array}{l}C_6H_5\\COHo\end{array}\right.}\qquad\qquad\underset{\text{Salicylic acid.}}{\left\{\begin{array}{l}C_6H_4Ho\\COHo\end{array}\right.}\;;$$

and the oil of meadow-sweet (*Spiræa ulmaria*) is generally regarded as the aldehyde of salicylic acid:—

$$\left\{\begin{array}{l}C_6H_4Ho\\COH\end{array}\right..$$

Oxymethyl-phenylformic acid is the lactic representative of toluylic acid, from which last-named acid it is prepared. Its constitution will be understood from the following graphic formula:—

$$\left\{\begin{array}{l}CH_2Ho\\C_6H_4\\COHo\end{array}\right. =$$



Oxymethyl-phenylformic acid.

The following acids also probably belong to the phenyl-lactic series:—

			Melting-point.
Isomeric.	Cresotic acid	$\left\{\begin{array}{l}C_7H_7O\\COHo\end{array}\right.$	153°.
	Anisic acid	$\left\{\begin{array}{l}C_6H_4Meo\\COHo\end{array}\right.$	175°.
	Paraphloretic acid	$\left\{\begin{array}{l}C_7H_6Meo\\COHo\end{array}\right.$	——
	Thymotic acid..............	$\left\{\begin{array}{l}C_{10}H_{13}O\\COHo\end{array}\right.$	120°.

BENZOIC ACID.

$$\left\{\begin{array}{l}C_6H_5\\ COHo\end{array}\right. .$$

Molecular weight =122. *Molecular volume* $\square\square$. 1 *litre of benzoic acid vapour weighs* 61 *criths. Fuses at* 121°·4. *Boils at* 239°.

Occurrence.—In many balsams and gums. In putrid urine.

Preparation.—1. By the oxidation of oil of bitter almonds (p. 112).

2. By the action of fused potassic hydrate on cinnamic acid:—

$$\underset{\text{Cinnamic acid.}}{\left\{\begin{array}{l}C(C_7H_6)''H\\ COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}CH_3\\ COKo\end{array}\right.} + \underset{\text{Potassic benzoate.}}{\left\{\begin{array}{l}C_6H_5\\ COKo\end{array}\right.} + H_2.$$

3. By boiling hippuric acid with hydrochloric acid:—

$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Glycollamic acid.}}{\left\{\begin{array}{l}CH_2(NH_2)\\ COHo\end{array}\right.} + \underset{\text{Benzoic acid.}}{\left\{\begin{array}{l}C_6H_5\\ COHo\end{array}\right.} .$$

4. By the action of oxidizing agents on casein or gelatin.

5. From gum benzoin, by sublimation, or by extraction with potassic hydrate and subsequent precipitation of the acid by hydrochloric acid.

6. Styrol treated with a solution of potassic permanganate gives benzoic acid and carbonic anhydride:—

$$\underset{\text{Styrol.}}{C_8H_8} + O_5 = \underset{\text{Benzoic acid.}}{\left\{\begin{array}{l}C_6H_5\\ COHo\end{array}\right.} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2}.$$

Gallic acid is a tetrahydric monobasic acid of the formula

$$\left\{\begin{array}{l}C_6H_2Ho_3\\ COHo\end{array}\right. .$$

It may therefore be regarded as benzoic acid in which three atoms of hydrogen have been replaced by three semimolecules of hydroxyl.

Tannic acid is obtained by the abstraction of one molecule of water from two molecules of gallic acid. Its constitutional formula is :—

$$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}_6H_2Ho_2\\ O\\ \mathbf{C}_6H_2Ho_2\\ \mathbf{C}OHo\end{array}\right. .$$

CHAPTER XXI.

THE ACIDS.

DIBASIC ACIDS.

General formula... $\mathbf{A}(COHo)_2$ or $\left\{\begin{array}{l}\mathbf{A}(COHo)\\ \mathbf{B}(COHo)\end{array}\right.$,

A and B being dyad radicals containing $C_nH_mO_l$.

These acids all contain two semimolecules of oxatyl ; and if in the general formula n, m, and l =0, oxalic acid will be the first term of the series.

Formation.—Many of the dibasic acids are produced by the oxidation of substances, the molecules of which are richer in carbon, such as oils and fats. Others are found ready formed in nature.

Reactions.—1. By the action of dehydrating substances, and even sometimes by heat alone, these acids lose water, forming anhydrides :—

$$\underset{\text{Acid.}}{\left\{\begin{array}{l}\mathbf{A}(COHo)\\ \mathbf{B}(COHo)\end{array}\right.} = \underset{\text{Water.}}{OH_2} + \underset{\text{Anhydride.}}{\left\{\begin{array}{l}\mathbf{A}(CO\\ \mathbf{B}(CO\end{array}O\right)}.$$

2. If the anhydride be submitted to the action of phosphoric chloride, an atom of oxygen is replaced by two of chlorine:—

$$\underset{\text{Anhydride.}}{\left\{\begin{matrix}\mathbf{A}(CO\\ \mathbf{B}(CO\end{matrix}O\right)} + \underset{\substack{\text{Phosphoric}\\ \text{chloride.}}}{PCl_5} = \underset{\text{Chloride.}}{\left\{\begin{matrix}\mathbf{A}(COCl)\\ \mathbf{B}(COCl)\end{matrix}\right.} + \underset{\substack{\text{Phosphoric}\\ \text{oxytrichloride.}}}{POCl_3}.$$

3. Both the anhydrides and the chlorides are reconverted into the acids by the action of water:—

$$\underset{\text{Chloride.}}{\left\{\begin{matrix}\mathbf{A}(COCl)\\ \mathbf{B}(COCl)\end{matrix}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Acid.}}{\left\{\begin{matrix}\mathbf{A}(COHo)\\ \mathbf{B}(COHo)\end{matrix}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl}.$$

The dibasic acids may be divided into the four following series:—

1. Succinic or acetoid series .... $\left\{\begin{matrix}C_nH_{2n}(COHo)\\ C_mH_{2m}(COHo)\end{matrix}\right.$.

In the first member of the series *m* = 0.

2. Fumaric or acryloid series ..... " $\left\{\begin{matrix}C_nH_{2n-1}(COHo)\\ C_nH_{2n-1}(COHo)\end{matrix}\right\}$.

3. Malic or lactoid series .... $\left\{\begin{matrix}C_nH_{2n-1}Ho(COHo)\\ C_nH_{2n}(COHo)\end{matrix}\right.$.

4. Tartaric or glyoxyloid series ... $\left\{\begin{matrix}C_nH_{2n-1}Ho(COHo)\\ C_nH_{2n-1}Ho(COHo)\end{matrix}\right\}$.

The first and second series are dibasic and *dihydric*; the third, dibasic and *trihydric*; and the fourth, dibasic and *tetrahydric*.

1. *THE SUCCINIC OR ACETOID SERIES.*

General formula... $\left\{\begin{matrix}\mathbf{C}OHo\\ C_nH_{2n}\\ C_mH_{2m}\\ \mathbf{C}OHo\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}OHo\\ C_nH_{2n}\\ \mathbf{C}OHo\end{matrix}\right.$.

In addition to oxalic acid (oxatyl) which many chemists regard as the first member of this series, the following are known:—

Malonic acid ……… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 140°.

Succinic acid ……… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 180°. Boils at 235°.

Isosuccinic acid …… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMeH}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 130°.

Pyrotartaric acid … $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_3H_6}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 112°. Boils at 200°.

Adipic acid ………… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_4H_8}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 140°.

Pimelic acid ……… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_5H_{10}}\\ \mathrm{COHo}\end{array}\right.$. *Fuses at 134°.*

Suberic acid ……. $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_6H_{12}}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 125°.

Anchoic acid ……… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_7H_{14}}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 116°.

Sebacic acid ………. $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_8H_{16}}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 127°.

Roccellic acid ……… $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C_{15}H_{30}}\\ \mathrm{COHo}\end{array}\right.$. Fuses at 132°. Boils at 200°.

It is obvious that there may be several modifications of each of these acids. Thus there are two succinic acids, one containing ethylene, and the other ethylidene (see p. 168):—

$$\left\{\begin{array}{l}\mathrm{CH_2(COHo)}\\ \mathrm{CH_2(COHo)}\end{array}\right. \text{ and } \left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH(COHo)_2}\end{array}\right.$$

1. *Relations of the Succinic to the Lactic Series of Acids and to the Glycols.*

These acids are related to the lactic series and to the glycols in the same way as the fatty acids are related to the monacid alcohols:—

$$\begin{array}{ccc}
\left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}H_2Ho\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}H_2Ho\\ \mathbf{C}OHo\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. . \\
\text{Glycol.} & \text{Glycollic acid.} & \text{Oxalic acid.}
\end{array}$$

This relation, however, does not strictly extend beyond the first member, although it may be partially traced in the relations of malonic and adipic acid to paralactic and paraleucic acid:—

$$\begin{array}{ccc}
\left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}H_2Ho)\\ \mathbf{C}H_2Ho\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}H_2Ho)\\ \mathbf{C}OHo\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}H_2(\mathbf{C}OHo)\\ \mathbf{C}OHo\end{matrix}\right. . \\
\text{Isopropylic glycol. (Unknown.)} & \text{Paralactic acid.} & \text{Malonic acid.} \\
\left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}H_2Ho)\\ \mathbf{C}H_2Ho\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}H_2Ho)\\ \mathbf{C}OHo\end{matrix}\right. . & \left\{\begin{matrix}\mathbf{C}_4H_8(\mathbf{C}OHo)\\ \mathbf{C}OHo\end{matrix}\right. . \\
\text{Unknown glycol.} & \text{Paraleucic acid.} & \text{Adipic acid.}
\end{array}$$

2. *Relations of the Succinic Series to the Dyad Radicals.*

1. The acids of the succinic series are intimately related to the dyad radicals, the nitriles or abnormal cyanides of which are readily converted into dibasic acids by ebullition with potassic hydrate or hydrochloric acid:—

$$\underset{\text{Abnormal cyanide of the dyad radical.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n}(\mathbf{C}N''')\\ \mathbf{C}_nH_{2n}(\mathbf{C}N''')\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Potassic salt of the dibasic acid.}}{\left\{\begin{matrix}\mathbf{C}_nH_{2n}(\mathbf{C}OKo)\\ \mathbf{C}_nH_{2n}(\mathbf{C}OKo)\end{matrix}\right.} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3}.$$

2. Some of these acids, when heated with excess of caustic baryta, give up two atoms of carbonic anhydride, yielding the hydrides of the dyad radicals:—

$$\underset{\text{Suberic acid.}}{\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}_6H_{12}\\ \mathbf{C}OHo\end{matrix}\right.} = \underset{\text{Carbonic anhydride.}}{2\mathbf{C}O_2} + (\mathbf{C}_6H_{12})''H_2.$$

$$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}_8H_{16}\\ \mathbf{C}OHo\end{matrix}\right. = 2\mathbf{C}O_2 + (C_8H_{16})''H_2.$$

Sebacic acid. Carbonic anhydride.

These reactions are the analogues, in the dyad series, of the process by which marsh-gas is obtained from acetic acid. The hydrides of the dyad radicals so obtained are isomeric with those of the corresponding monad radicals.

The elimination of carbonic anhydride from a monobasic acid can only take place once, while from a dibasic acid it takes place in two successive stages :—

In the case of a monobasic acid,

$$\left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}OHo\end{matrix}\right. - \mathbf{C}O_2 = \mathbf{C}_nH_{2n+1}H.$$

In the case of a dibasic acid,

$$\text{1st stage} \ldots \left\{\begin{matrix}\mathbf{C}_nH_{2n}(\mathbf{C}OHo)\\ \mathbf{C}_nH_{2n}(\mathbf{C}OHo)\end{matrix}\right. - \mathbf{C}O_2 = \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n}\\ \mathbf{C}OHo\end{matrix}\right. :$$

$$\text{2nd stage} \ldots \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n}\\ \mathbf{C}OHo\end{matrix}\right. - \mathbf{C}O_2 = \left\{\begin{matrix}\mathbf{C}_nH_{2n+1}\\ \mathbf{C}_nH_{2n+1}\end{matrix}\right. .$$

8. *Relations of the Succinic to the Acetic Series of Acids.*

1. By the loss of the elements of carbonic anhydride, the first three members of the succinic series are converted into members of the acetic series, containing one atom of carbon less :—

$$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right. = \mathbf{C}O_2 + \left\{\begin{matrix}H\\ \mathbf{C}OHo\end{matrix}\right. .$$

Oxalic acid. Carbonic anhydride. Formic acid.

$$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{matrix}\right. = \mathbf{C}O_2 + \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right. .$$

Malonic acid. Carbonic anhydride. Acetic acid.

$$\underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right.} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Propionic acid.}}{\left\{\begin{array}{l}CMeH_2\\COHo\end{array}\right.}.$$

In the first two cases the action of heat alone is sufficient to effect the transformation; but in the third the affinity of lime for carbonic anhydride must be superadded.

2. Conversely, the members of the acetic series may be converted into those of the succinic containing one atom of carbon more, by replacing one atom of the hydrogen in the positive radical of the acid by cyanogen, and then boiling with potassic hydrate:—

$$\underset{\text{Cyanacetic acid.}}{\left\{\begin{array}{l}CH_2(CN''')\\COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic malonate.}}{\left\{\begin{array}{l}CH_2(COKo)\\COKo\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3}.$$

The conversion of formic acid into oxalic acid, by heating with potassic hydrate, also belongs to this class of reactions:—

$$\underset{\text{Formic acid.}}{2\left\{\begin{array}{l}H\\COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}COKo\\COKo\end{array}\right.} + \underset{\text{Water.}}{2OH_2} + H_2.$$

SUCCINIC ACID.

$$\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right..$$

Fuses at 180°. *Boils at* 235°. *Dissolves in* 20 *parts of cold water*.

Occurrence.—In amber; in some kinds of lignite; in the resin of some kinds of pine; also in many other vegetable and animal substances.

Formation.—1. By the action of potassic hydrate upon abnormal ethylenic cyanide (p. 161): this reaction proves that succinic acid contains ethylene, and that its constitutional formula is as given above.

2. By the oxidation of butyric acid by nitric acid:—

$$\underset{\text{Butyric acid.}}{\left\{\begin{array}{l}CEtH_2\\COHo\end{array}\right.} + O_3 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

The nature of this reaction is more clearly seen with fully developed formulæ, thus:—

$$\underset{\text{Butyric acid.}}{\left\{\begin{array}{l}CH_3\\CH_2\\CH_2\\COHo\end{array}\right.} + O_3 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

3. By the reduction of malic acid by fermentation, or by hydriodic acid:—

$$\underset{\text{Malic acid.}}{\left\{\begin{array}{l}COHo\\CHHo\\CH_2\\COHo\end{array}\right.} + H_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

4. By the reduction of tartaric acid by hydriodic acid:—

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}COHo\\CHHo\\CHHo\\COHo\end{array}\right.} + \underset{\text{Hydriodic acid.}}{4HI} = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right.} + \underset{\text{Water.}}{2OH_2} + 2I_2.$$

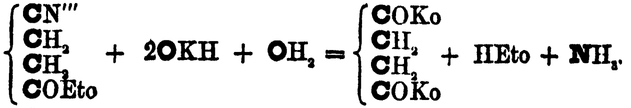
It is evident that this reaction is perfectly analogous to that by which lactic acid is transformed into propionic acid (p. 125).

5. The two isomeric acids, fumaric and maleic acids, are converted by nascent hydrogen into succinic acid:—

$$\begin{array}{l}\{COHo\\ ''\left\{\begin{array}{l}CH\\CH\end{array}\right.\\ \{COHo\end{array} + H_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right.}.$$

$$\left\{\begin{array}{l}COHo\\CH_2\\''C\\COHo\end{array}\right. + H_2 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}COHo\\CH_2\\CH_2\\COHo\end{array}\right.}.$$

6. By boiling ethylic β cyanopropionate with solution of caustic potash:—

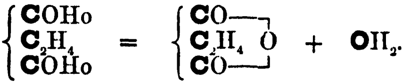


$$\left\{\begin{array}{l}CN'''\\CH_2\\CH_2\\COEto\end{array}\right. + 2OKH + OH_2 = \left\{\begin{array}{l}COKo\\CH_2\\CH_2\\COKo\end{array}\right. + HEto + NH_3.$$

Ethylic β cyanopropionate. Succinic acid. Alcohol. Ammonia.

The two processes by which succinic acid is generally prepared are, the distillation of amber and the fermentation of calcic malate.

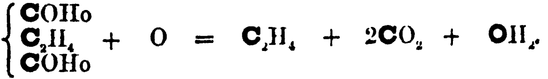
Reactions.—1. By distillation, succinic acid splits almost entirely into succinic anhydride and water:—



$$\left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right. = \left\{\begin{array}{l}CO\\C_2H_4\\CO\end{array}\right\}O + OH_2.$$

Succinic acid. Succinic anhydride. Water.

2. Under the action of nascent oxygen produced by electrolysis, succinic acid yields ethylene, carbonic anhydride, and water:—

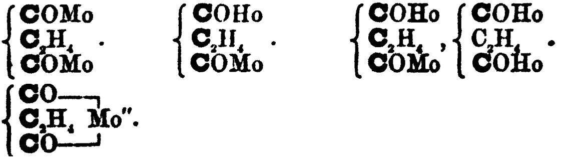


$$\left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right. + O = C_2H_4 + 2CO_2 + OH_2.$$

Succinic acid. Ethylene. Carbonic anhydride. Water.

3. Succinic acid may be boiled for hours with concentrated nitric acid without suffering any change; neither is it affected by a mixture of potassic chlorate and hydrochloric acid; but it produces acetic acid when distilled with sulphuric acid and manganic oxide.

4. Succinic acid forms three kinds of salts, viz.:—



Normal. Acid. Superacid.

$$\left\{\begin{array}{l}COMo\\C_2H_4\\COMo\end{array}\right. . \quad \left\{\begin{array}{l}COHo\\C_2H_4\\COMo\end{array}\right. . \quad \left\{\begin{array}{l}COHo\\C_2H_4\\COMo\end{array}\right. , \left\{\begin{array}{l}COHo\\C_2H_4\\COHo\end{array}\right. .$$

$$\left\{\begin{array}{l}CO\\C_2H_4\\CO\end{array}\right\}Mo''.$$

ISOSUCCINIC ACID.

$$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{MeH}\,.\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$$

Fuses at 130°. *Dissolves in* 5·4 *parts of cold water.*

Formation.—By boiling ethylic *a* cyanopropionate with solution of caustic potash:—

$$\underset{\substack{\text{Ethylic}\\ a\ \text{cyanopropionate.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{N}'''\\ \mathbf{C}\mathrm{MeH}\\ \mathbf{C}\mathrm{OEto}\end{array}\right.} + 2\mathbf{O}\mathrm{KH} + \mathbf{O}\mathrm{H}_2 = \underset{\substack{\text{Succinic}\\ \text{acid.}}}{\left\{\begin{array}{l}\mathbf{C}\mathrm{OKo}\\ \mathbf{C}\mathrm{MeH}\\ \mathbf{C}\mathrm{OKo}\end{array}\right.} + \underset{\text{Alcohol.}}{\mathrm{HEto}} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H}_3}.$$

CHAPTER XXII.

THE ACIDS.

2. *FUMARIC OR ACRYLOID SERIES.*

General formula ...$''\left\{\begin{array}{l}\mathbf{C}_n\mathrm{H}_{2n-1}(\mathrm{COHo})\\ \mathbf{C}_n\mathrm{H}_{2n-1}(\mathrm{COHo})\end{array}\right.$ or $\mathbf{C}_n\mathrm{H}_{2n-2}(\mathrm{COHo})_2$.

In this series there are three isomeric acids containing four atoms of carbon, viz.

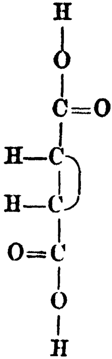
$$\begin{array}{ll} & \text{Formula.}\\ \left.\begin{array}{l}\text{Fumaric acid}\\ \text{Maleic acid}\\ \text{Isomaleic acid}\end{array}\right\} & \ldots\ \ldots''\mathbf{C}''_2\mathrm{H}_2(\mathrm{COHo})_2\,;\end{array}$$

and three other isomeric acids containing five atoms of carbon, viz.

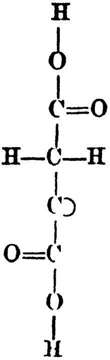
$$\left.\begin{array}{l}\text{Itaconic acid}\\ \text{Citraconic acid}\\ \text{Mesaconic acid}\end{array}\right\}\ldots\ldots{}^{\mathrm{vi}}(\mathbf{C}_3)^{\mathrm{vi}}\mathrm{H}_4(\mathrm{COHo})_2.$$

Constitutional notation predicts the existence of a fourth acid belonging to the four-carbon group. The following are the four possible formulæ for these acids:—

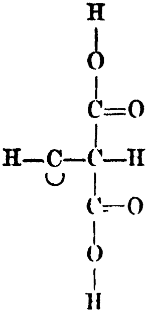
No. 1.



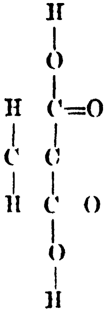
No. 2.



No. 3.



No. 4.



$$\begin{array}{l}\{\mathrm{COHo}\\ {}''\left\{\begin{array}{l}\mathrm{CH}\\ \mathrm{CH}\end{array}\right.\\ \{\mathrm{COHo}\end{array} \cdot \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ {}''\mathrm{C}\\ \mathrm{COHo}\end{array}\right. \cdot \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{C(''CH)H.}\\ \mathrm{COHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMe''.}\\ \mathrm{COHo}\end{array}\right.$$

Of these formulæ, Nos. 1 and 2 represent fumaric and maleic acids. Data are still wanting to enable its own particular formula to be assigned to each of these acids; but the first two formulæ must belong to fumaric and maleic acids, because both these acids yield succinic acid under the influence of nascent hydrogen, thus:—

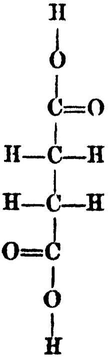
No. 1.

$$\begin{array}{l}\{\mathrm{COHo}\\ {}''\left\{\begin{array}{l}\mathrm{CH}\\ \mathrm{CH}\end{array}\right.\\ \{\mathrm{COHo}\end{array} + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$$

No. 2.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ {}''\mathrm{C}\\ \mathrm{COHo}\end{array}\right. + \mathrm{H_2} = \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$$

Succinic acid.



Succinic acid.

That succinic acid contains ethylene $\left({}'' \left\{ \begin{matrix} CH_2 \\ CH_2 \end{matrix} \right. \right)$ and not ethylidene $\left(\left\{ \begin{matrix} CH_3 \\ {}''CH \end{matrix} \right. \right)$, is proved by its formation from abnormal ethylenic cyanide (p. 161); but formulæ Nos. 3 and 4 give, by the addition of two atoms of hydrogen, the formula of isosuccinic acid containing ethylidene, thus:—

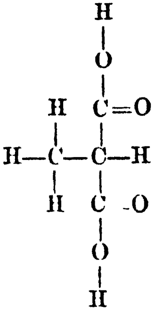
No. 3.

$$\left\{ \begin{matrix} COHo \\ C(''CH)H \\ COHo \end{matrix} \right. + H_2 = \left\{ \begin{matrix} COHo \\ CMeH. \\ COHo \end{matrix} \right.$$

No. 4.

$$\left\{ \begin{matrix} COHo \\ CMe'' \\ COHo \end{matrix} \right. + H_2 = \left\{ \begin{matrix} COHo \\ CMeH. \\ COHo \end{matrix} \right.$$

Isosuccinic acid.

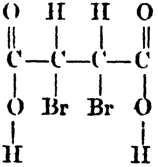


Isosuccinic acid.

Fumaric acid combines directly with bromine, producing dibromosuccinic acid. Malcic acid also combines directly with bromine, producing isodibromosuccinic acid. The following formulæ show the nature of this isomerism:—

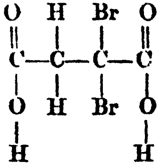
Corresponding to No. 1.

$$\left\{ \begin{matrix} COHo \\ CHBr \\ CHBr \\ COHo \end{matrix} \right.$$



Corresponding to No. 2.

$$\left\{ \begin{matrix} COHo \\ CH_2 \\ CBr_2 \\ COHo \end{matrix} \right.$$



When acted upon by nascent hydrogen, both these isomeric bromo-acids produce, as might be expected, the same succinic acid:—

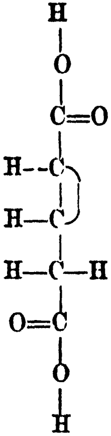
$$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}HBr\\ \mathbf{C}HBr\\ \mathbf{C}OHo\end{array}\right. + H_4 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Hydrobromic acid.}}{2HBr}:$$

$$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}H_2\\ \mathbf{C}Br_2\\ \mathbf{C}OHo\end{array}\right. + H_4 = \underset{\text{Succinic acid.}}{\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}H_2\\ \mathbf{C}H_2\\ \mathbf{C}OHo\end{array}\right.} + \underset{\text{Hydrobromic acid.}}{2HBr}.$$

Inasmuch as formulæ Nos. 1 and 2 belong to fumaric and maleic acids, it follows that one of the two remaining constitutional formulæ must be that of isomaleic acid. It is impossible at present to determine which of these formulæ is to be assigned to this acid; but in any case there can scarcely be a doubt that isomaleic acid, when treated with nascent hydrogen, will yield isosuccinic acid, as shown above.

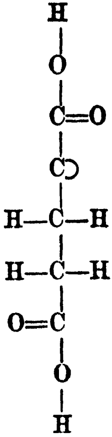
Of a similar character is the relation subsisting between the isomeric acids of this series containing five atoms of carbon, viz. itaconic acid, citraconic acid, and mesaconic acid. There are no less than eleven possible formulæ for this five-carbon group of acids; but the three individual formulæ belonging to the three known acids cannot at present be determined. The following four formulæ will serve as specimens of the whole, and as illustrations of the cause of isomerism in these acids:—

No. 1.



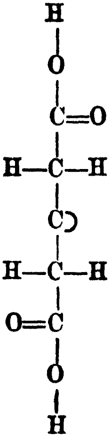
$$\left\{\begin{array}{l}COHo\\ CH\\ CH\\ CH_2\\ COHo\end{array}\right.$$

No. 2.



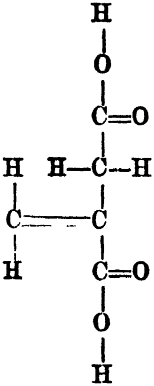
$$\left\{\begin{array}{l}COHo\\ {}''C\\ CH_2\\ CH_2\\ COHo\end{array}\right.$$

No. 3.



$$\left\{\begin{array}{l}COHo\\ CH_2\\ {}''C\\ CH_2\\ COHo\end{array}\right.$$

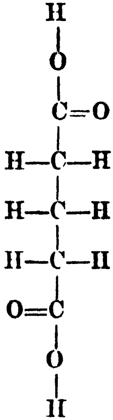
No. 4.



$$\left\{\begin{array}{l}COHo\\ CH_2\\ CMe''\\ COHo\end{array}\right.$$

Itaconic, citraconic, and mesaconic acids stand in the same relation to pyrotartaric acid as fumaric and maleic acids occupy with regard to succinic acid; for, when submitted to the action of nascent hydrogen, they all yield the same pyrotartaric acid; and it is therefore highly probable that the first three of the above formulæ belong to these acids. The formula of pyrotartaric acid is

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$$



Treated with bromine, the three acids yield three isomeric brominated acids, which are transformed by nascent hydrogen into the same pyrotartaric acid.

By the action of hypochlorous acid on itaconic acid and subsequent replacement of the chlorine by hydroxyl, itatartaric acid is formed:—

$$\left\{\begin{array}{l}\mathrm{COHo}\\ {}''\!\left\{\begin{array}{l}\mathrm{CH}\\ \mathrm{CH}\end{array}\right.\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHCl}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right.$$

Itaconic acid. Itatartaric acid.

Itatartaric acid, by distillation at 125°, gives carbonic anhydride, water, and pyroitauvic acid, which appears to belong both to the lactic and the acrylic series of acids.

$$\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. = \mathrm{CO_2} + \mathrm{OH_2} + \left\{\begin{array}{l}{}''\!\left\{\begin{array}{l}\mathrm{CHHo}\\ \mathrm{CH}\end{array}\right.\\ \mathrm{CH_2}\\ \mathrm{COHo}\end{array}\right. .$$

Itatartaric acid. Pyroitauvic acid.

CHAPTER XXIII.

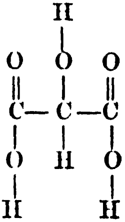
THE ACIDS.

3. *MALIC OR LACTOID SERIES.*

General formula...... $\left\{\begin{matrix} C_nH_{2n-1}Ho(COHo) \\ C_nH_{2n}(COHo) \end{matrix}\right.$ or $\left\{\begin{matrix} COHo \\ C_nH_{2n-1}Ho. \\ COHo \end{matrix}\right.$

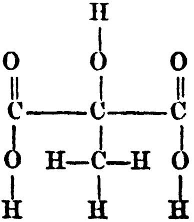
Only two acids belonging to this series are known, viz. tartronic acid and malic acid. Like lactic acid, they both contain a semimolecule of *non-oxatylic* hydroxyl:—

Tartronic acid.. ... $\left\{\begin{matrix} COHo \\ CHHo. \\ COHo \end{matrix}\right.$



This acid may be regarded as the product of the oxidation of glycerin, although it has not yet been so produced. It is obtained by the gentle oxidation of tartaric acid (p. 175).

Malic acid ...... $\left\{\begin{matrix} COHo \\ CMeHo. \\ COHo \end{matrix}\right.$



Malic acid may be viewed as the product of the oxidation of the hitherto undiscovered butyl glycerin, $\left\{\begin{matrix} CH_2Ho \\ CMeHo. \\ CH_2Ho \end{matrix}\right.$

This acid is contained in apples, and in many other fruits.

When gently heated with potassic hydrate, hydrogen is evolved, potassic oxalate and acetate being produced:—

$$\underset{\text{Potassic malate.}}{\left\{\begin{array}{l}\mathrm{COKo}\\ \mathrm{CMeHo}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic hydrate.}}{\mathrm{KHo}} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}\mathrm{COKo}\\ \mathrm{COKo}\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COKo}\end{array}\right.} + \mathrm{H_2}.$$

4. *TARTARIC OR GLYOXYLOID SERIES.*

This series contains at present only two members; but these have numerous isomers, which have been studied, however, only in the case of the first. Like the glyoxylic series, these acids contain two semimolecules of *non-oxatylic* hydroxyl.

Tartaric acid .... $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{COHo}\end{array}\right.$

Homotartaric or glycomalic acid .... $\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{COHo}\end{array}\right.$

There are four possible constitutional formulæ for tartaric acid; viz.:—

$$\overset{\text{A.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{COHo}\end{array}\right.} \quad \overset{\text{B.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CH_2}\\ \mathrm{CHo_2}\\ \mathrm{COHo}\end{array}\right.} \quad \overset{\text{C.}}{\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHo(COHo)}.\\ \mathrm{COHo}\end{array}\right.} \quad \overset{\text{D.}}{\left\{\begin{array}{l}\mathrm{CHHo_2}\\ \mathrm{CH(COHo)}.\\ \mathrm{COHo}\end{array}\right.}$$

The known varieties of tartaric acid are also limited to four, viz.:—

1. Dextrotartaric or common tartaric acid, so called from its property of causing the plane of polarization of a ray of light to rotate to the right.

2. Lævotartaric acid, which turns the plane of polarization to the left.

3. Inactive tartaric acid, which does not affect the plane of polarization.

4. Metatartaric acid.

It has been already shown (p. 164) that dextrotartaric acid yields succinic acid under the influence of hydriodic acid, whilst it has also been ascertained that inactive tartaric acid likewise produces succinic acid under the same circumstances. These reactions indicate A. and B. to be the formulæ of the dextro- and inactive tartaric acids. The formulæ C. and D. possibly belong to lævo- and metatartaric acids, in which case these acids, when treated with hydriodic acid, ought to yield isosuccinic acid. Thus—

$$\left\{\begin{array}{l}\mathrm{CH_2Ho}\\ \mathrm{CHo(COHo)}\\ \mathrm{COHo}\end{array}\right. + 4\mathrm{HI} = 2\mathrm{OH_2} + 2\mathrm{I_2}$$

$$+ \underset{\text{Isosuccinic acid}}{\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH(COHo)}\\ \mathrm{COHo}\end{array}\right.} \quad \text{or} \quad \left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CMeH}.\\ \mathrm{COHo}\end{array}\right.$$

Racemic acid is a compound of dextro- and lævotartaric acid. It may be produced by uniting them, and may again be resolved into them.

Inactive tartaric acid cannot be resolved into dextro- and lævo-tartaric acids.

It may be obtained by the action of water on argentic dibromosuccinate:—

$$\underset{\text{Argentic dibromosuccinate.}}{\left\{\begin{array}{l}\mathrm{COAgo}\\ \mathrm{CHBr}\\ \mathrm{CHBr}\\ \mathrm{COAgo}\end{array}\right.} + \underset{\text{Water.}}{2\mathrm{OH_2}} = \underset{\text{Inactive tartaric acid.}}{\left\{\begin{array}{l}\mathrm{COHo}\\ \mathrm{CHHo}\\ \mathrm{CHHo}\\ \mathrm{COHo}\end{array}\right.} + \underset{\text{Argentic bromide.}}{2\mathrm{AgBr}}.$$

The converse of this reaction is the transformation of tartaric acid into succinic acid by means of hydriodic acid (see p. 164).

Metatartaric acid is produced by fusing dextrotartaric acid.

Reactions.—1. Dextrotartaric acid, when treated with powerful oxidizing agents, gives formic acid.

2. Under the influence of very gentle oxidizing agents, tartronic acid is formed:—

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}COHo\\CHHo\\CHHo\\COHo\end{array}\right.} + O_2 = \underset{\text{Tartronic acid.}}{\left\{\begin{array}{l}COHo\\CHHo\\COHo\end{array}\right.} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2}$$

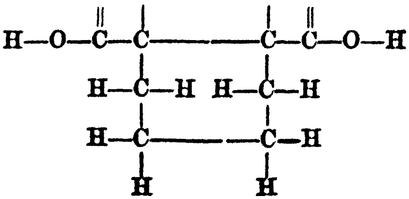
3. Heated with fused potassic hydrate, tartaric acid gives potassic oxalate and acetate, but without evolution of hydrogen:—

$$\underset{\text{Tartaric acid.}}{\left\{\begin{array}{l}COHo\\CHHo\\CHHo\\COHo\end{array}\right.} + \underset{\text{Potassic hydrate.}}{3KHo} = \underset{\text{Potassic oxalate.}}{\left\{\begin{array}{l}COKo\\COKo\end{array}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{array}{l}CH_3\\COKo\end{array}\right.} + \underset{\text{Water.}}{3OH_2}.$$

OTHER SERIES OF DIBASIC ACIDS.

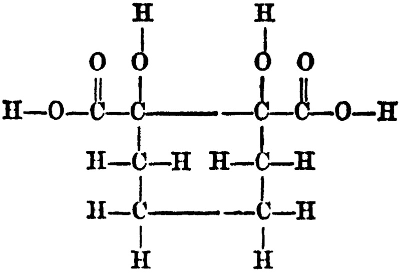
There is evidence of the existence of other series of dibasic acids, which may be regarded as derivatives of benzole or as the hexacarbon representatives of the succinic, fumaric, and tartaric series. The following are examples:—

$C_6H_{10}(COHo)_2$.



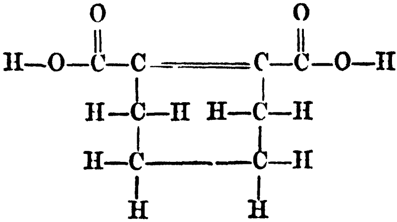
Hexahydrophthalic acid (Hexacarbon-succinic series).

$\mathbf{C}_6H_8Ho_2(COHo)_2$.



Tartrophthalic acid (Hexacarbon-tartaric series).

$\mathbf{C}_6H_8(COHo)_2$.



Tetrahydrophthalic acid (Hexacarbon-fumaric series).

The existence of another series of dibasic acids derived from hydrocarbons of a C_nH_{2n-18} series is indicated by the formation of *anthraquinonic acid*, which is identical with *alizarin*, the chief colouring-matter of the madder root. By oxidation, *anthracene* $(C_{14}H_{10})$ yields *anthraquinone* $(C_{14}H_8O_2)$, which, when heated strongly with sulphuric acid, is converted into *disulphanthraquinonic acid*, which has probably the following constitution :—

$$\left\{\begin{array}{l}\mathbf{C}O(S^{iv}O_2Ho)\\ (\mathbf{C}_{14}H_6)''\\ \mathbf{C}O(S^{iv}O_2Ho)\end{array}\right. .$$

When disulphanthraquinonic acid is heated with potassic hydrate to a temperature of about 180° C., it becomes intensely coloured, and is found to be converted into potassic alizarate (potassic anthraquinonate) :—

$$\underset{\text{Disulphanthraquinonic acid.}}{\left\{\begin{array}{l}\mathbf{C}O(S^{iv}O_2Ho)\\(\mathbf{C}_{12}H_6)''\\\mathbf{C}O(S^{iv}O_2Ho)\end{array}\right.} + \underset{\text{Potassic hydrate.}}{6\mathbf{O}KH} = \underset{\text{Potassic alizarate.}}{\left\{\begin{array}{l}\mathbf{C}OKo\\(\mathbf{C}_{12}H_6)''\\\mathbf{C}OKo\end{array}\right.} + \underset{\text{Potassic sulphite.}}{2\mathbf{S}OKo_2}$$

$$+ \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

On the addition of an acid to an aqueous solution of potassic alizarate, alizaric acid ($\mathbf{C}_{12}H_6(\mathbf{C}OHo)_2$), identical in properties with the natural alizarin of madder root, is precipitated.

Anthraflavic acid ($\mathbf{C}_{12}H_6(\mathbf{C}OHo)_2$), isomeric with alizaric acid, but possessing no tinctorial properties, is usually simultaneously formed in the above reactions.

CHAPTER XXIV.

THE ACIDS.

TRIBASIC ACIDS.

The tribasic acids all contain three semimolecules of oxatyl. They may be divided into the following three series, each series being, however, at present only represented by one acid.

1. Tricarballylic or acetoid series :—

$$\text{Tricarballylic acid} \ldots \left\{\begin{array}{l}\mathbf{C}H_2(\mathbf{C}OHo)\\\mathbf{C}H(\mathbf{C}OHo)\\\mathbf{C}H_2(\mathbf{C}OHo)\end{array}\right. .$$

2. Aconitic or acryloid series :—

$$\text{Aconitic acid} \ldots\ldots\ldots\ {}''\left\{\begin{array}{l}\mathbf{C}H(\mathbf{C}OHo)\\\mathbf{C}(\mathbf{C}OHo)\\\mathbf{C}H_2(\mathbf{C}OHo)\end{array}\right. .$$

3. Citric or lactoid series :—

$$\text{Citric acid}\ldots\ldots\ldots\ldots\ \left\{\begin{array}{l}\textbf{C}\text{HHo(COHo)}\\ \textbf{C}\text{H(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. .$$

Tricarballylic acid is trihydric. It is obtained from glycerin by replacing the hydroxyl in the latter by cyanogen, and then acting upon the tricyanhydrin, so formed, by potassic hydrate :—

$$\left\{\begin{array}{l}\textbf{C}\text{H}_2\text{(CN}'''\text{)}\\ \textbf{C}\text{H(CN}'''\text{)}\\ \textbf{C}\text{H}_2\text{(CN}'''\text{)}\end{array}\right. + 3\text{KHo} + 3\textbf{O}\text{H}_2 = \left\{\begin{array}{l}\textbf{C}\text{H}_2\text{(COKo)}\\ \textbf{C}\text{H(COKo)}\\ \textbf{C}\text{H}_2\text{(COKo)}\end{array}\right. + 3\textbf{N}\text{H}_3.$$

Tricyanhydrin. Potassic hydrate. Water. Potassic tricarballylate. Ammonia.

Aconitic acid (*equisetic acid*, *citridic acid*) is also trihydric. It is found in the roots and leaves of monkshood, and may also be obtained by heating citric acid. Aconitic acid is also produced by the action of hydrobromic acid upon citric acid, the reaction taking place in the two following stages :—

$$\left\{\begin{array}{l}\textbf{C}\text{HHo(COHo)}\\ \textbf{C}\text{H(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. + \text{HBr} = \left\{\begin{array}{l}\textbf{C}\text{HBr(COHo)}\\ \textbf{C}\text{H(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. + \textbf{O}\text{H}_2;$$

Citric acid. Bromotricarballylic acid. Water.

$$\left\{\begin{array}{l}\textbf{C}\text{HBr(COHo)}\\ \textbf{C}\text{H(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. = {}''\left\{\begin{array}{l}\textbf{C}\text{H(COHo)}\\ \textbf{C}\text{(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. + \text{HBr}.$$

Bromotricarballylic acid. Aconitic acid.

Heated to 160°, aconitic acid is converted into itaconic acid :—

$$''\left\{\begin{array}{l}\textbf{C}\text{H(COHo}\\ \textbf{C}\text{(COHo)}\\ \textbf{C}\text{H}_2\text{(COHo)}\end{array}\right. = \begin{array}{l}''\left\{\begin{array}{l}\textbf{C}\text{OHo}\\ \textbf{C}\text{H}\\ \textbf{C}\text{H}\end{array}\right.\\ \left\{\begin{array}{l}\textbf{C}\text{H}_2\\ \textbf{C}\text{OHo}\end{array}\right.\end{array} + \textbf{C}\text{O}_2.$$

Aconitic acid. Itaconic acid. Carbonic anhydride.

Citric acid is tetrahydric, and contains, therefore, like lactic acid, one semimolecule of *non-oxatylic* hydroxyl. It is found in the free state in oranges, lemons, citrons, and many other fruits, also in the potato and the onion. By the graduated application of heat, citric acid yields aconitic, itaconic, and citraconic acids. At the earlier stage of the decomposition it also yields acetone. Heated with fused potassic hydrate it gives potassic oxalate and acetate:—

$$\underset{\text{Citric acid.}}{\left\{\begin{array}{l}\mathrm{CHHo(COHo)}\\\mathrm{CH(COHo)}\\\mathrm{CH_2(COHo)}\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{\mathrm{4KHo}} = \underset{\substack{\text{Potassic}\\\text{oxalate.}}}{\left\{\begin{array}{l}\mathrm{COKo}\\\mathrm{COKo}\end{array}\right.} + \underset{\substack{\text{Potassic}\\\text{acetate.}}}{2\left\{\begin{array}{l}\mathrm{CH_3}\\\mathrm{COKo}\end{array}\right.} + \underset{\text{Water.}}{\mathrm{3OH_2}}.$$

By being heated with hydriodic acid, citric acid is transformed into tricarballylic acid:—

$$\underset{\text{Citric acid.}}{\left\{\begin{array}{l}\mathrm{CHHo(COHo)}\\\mathrm{CH(COHo)}\\\mathrm{CH_2(COHo)}\end{array}\right.} + \mathrm{2HI} = \underset{\text{Tricarballylic acid}}{\left\{\begin{array}{l}\mathrm{CH_2(COHo)}\\\mathrm{CH(COHo)}\\\mathrm{CH_2(COHo)}\end{array}\right.} + \underset{\text{Water}}{\mathrm{OH_2}} + \mathrm{I_2}.$$

Desoxalic acid is closely connected with citric acid; it is hexahydric, and may be regarded as citric acid in which two atoms of *non-oxatylic* hydrogen have been replaced by hydroxyl. Its constitutional formula is probably

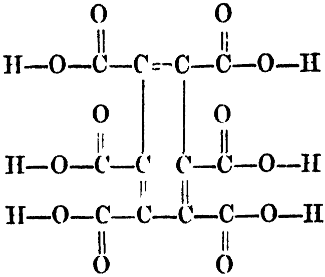
$$\left\{\begin{array}{l}\mathrm{CHHo(COHo)}\\\mathrm{CHo(COHo)}\\\mathrm{CHHo(COHo)}\end{array}\right. .$$

It is obtained from the product of the action of sodium upon oxalic ether.

TETRABASIC AND HEXABASIC ACIDS.

Pyromellitic acid ($\mathrm{C_6H_2(COHo)_4}$) and ***mellitic acid*** ($\mathrm{C_6(COHo)_6}$) are instances of acids of these degrees of basicity; and it can scarcely be doubted that an intermediate pentabasic acid will be found to exist. The following graphic formula of mellitic acid shows the relation of this acid to benzol, and indicates the constitutional formulæ of the other acids built upon the same type and mentioned below:—

Mellitic acid.



Five out of the six possible acids thus related to benzole are now known. Their names and formulæ are given in the following Table:—

Benzoic acid	$C_6H_5(COHo)$.
Phthalic acid Isophthalic acid Terephthalic acid	$C_6H_4(COHo)_2$.
Trimellitic acid Trimesic acid Hemimellitic acid	$C_6H_3(COHo)_3$.
Pyromellitic acid Prehnitic acid Mellophanic acid	$C_6H_2(COHo)_4$.
Unknown acid	$C_6H(COHo)_5$.
Mellitic acid	$C_6(COHo)_6$.

CHAPTER XXV.

THE ANHYDRIDES.

The anhydrides are compounds obtained from the acids by the abstraction of the hydrogen of their hydroxyl, together with sufficient oxygen to form water.

For every two atoms of hydrogen and one of oxygen thus abstracted from hydroxyl, there will obviously remain one atom of oxygen, which, as a dyad element, exactly satisfies the two bonds vacated by the hydroxyl:—

$$\underset{\text{Hydroxyl.}}{2Ho} = \underset{\text{Water.}}{OH_2} + O''.$$

On this account, two molecules of a monohydric acid are required to form one molecule of anhydride, thus:—

$$\underset{\text{Acetic acid.}}{2CMeOHo} = \underset{\text{Acetic anhydride.}}{\left\{\begin{array}{l}CMeO\\O\\CMeO\end{array}\right.} + \underset{\text{Water.}}{OH_2}.$$

The anhydrides of those monobasic and dibasic acids which contain one and two semimolecules of hydroxyl have alone been investigated.

They may be divided into the following classes:—

1. Anhydrides of the monohydric monobasic acids .... $\left\{\begin{array}{l}C_nH_{2n+1}\\CO\\O\\CO\\C_nH_{2n+1}\end{array}\right.$ and $\left\{\begin{array}{l}C_nH_{2n-7}\\CO\\O\\CO\\C_nH_{2n-7}\end{array}\right.$.

2. Anhydrides of the dihydric monobasic acids .... $\left\{\begin{array}{l}C(C_nH_{2n+1})_2\\CO\end{array}\right\}O.$

3. Anhydrides of the dihydric dibasic acids .... $\left\{\begin{array}{l}CO—\\C_nH_{2n}\ \ O.\\CO—\end{array}\right.$

1. *ANHYDRIDES OF THE MONOHYDRIC MONOBASIC ACIDS.*

These are known only in the acetic and benzoic series.

They bear the same relation to the acids from which they are derived as that borne by the ethers to the alcohols.

The residues of different acids unite to form mixed anhydrides anologous to the mixed ethers. Aceto-benzoic anhydride is a body of this class.

Formation.—By the action of the chloracids, or so-called chlorides of the monad negative radicals, on the potassic salts of the acids:—

$$\mathbf{C}(C_nH_{2n+1})OKo + \mathbf{C}(C_nH_{2n+1})OCl = \left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})O\\ O\\ \mathbf{C}(C_nH_{2n+1})O\end{matrix}\right. + KCl.$$

Potassic salt. Chloracid. Anhydride. Potassic chloride.

Reaction. In contact with water they are converted into the corresponding acids:—

$$\left\{\begin{matrix}\mathbf{C}(C_nH_{2n+1})O\\ O\\ \mathbf{C}(C_nH_{2n+1})O\end{matrix}\right. + OH_2 = 2\mathbf{C}(C_nH_{2n+1})OHo.$$

Anhydride. Water. Acid.

The following is a list of the anhydrides belonging to this class:—

				Fusing-point.	Boiling point.
Acetic anhydride	$\left\{\begin{matrix}\mathbf{C}MeO\\ O\\ \mathbf{C}MeO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(CH_3)O\\ O\\ \mathbf{C}(CH_3)O\end{matrix}\right.$	——	138°.
Propionic anhydride ...	$\left\{\begin{matrix}\mathbf{C}EtO\\ O\\ \mathbf{C}EtO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(C_2H_5)O\\ O\\ \mathbf{C}(C_2H_5)O\end{matrix}\right.$	——	165°.
Butyric anhydride......	$\left\{\begin{matrix}\mathbf{C}PrO\\ O\\ \mathbf{C}PrO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(C_3H_7)O\\ O\\ \mathbf{C}(C_3H_7)O\end{matrix}\right.$	——	about 190°.
Valeric anhydride	$\left\{\begin{matrix}\mathbf{C}BuO\\ O\\ \mathbf{C}BuO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(C_4H_9)O\\ O\\ \mathbf{C}(C_4H_9)O\end{matrix}\right.$	——	about 215°.

				Fusing-point.	Boiling-point.
Caproic anhydride	$\left\{\begin{matrix}\mathbf{C}AyO\\O\\\mathbf{C}AyO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(C_5H_{11})O\\O\\\mathbf{C}(C_5H_{11})O\end{matrix}\right.$	—	—
Œnanthylic anhydride	$\left\{\begin{matrix}\mathbf{C}CpO\\O\\\mathbf{C}CpO\end{matrix}\right.$	or	$\left\{\begin{matrix}\mathbf{C}(C_6H_{13})O\\O\\\mathbf{C}(C_6H_{13})O\end{matrix}\right.$	42°.	310°.
Benzoic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_6H_5)O\\O\\\mathbf{C}(C_6H_5)O\end{matrix}\right.$			—	—
Acetobenzoic anhydride	$\left\{\begin{matrix}\mathbf{C}MeO\\O\\\mathbf{C}(C_6H_5)O\end{matrix}\right.$			—	120°.
Caprylic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_7H_{15})O\\O\\\mathbf{C}(C_7H_{15})O\end{matrix}\right.$			below 0°.	about 290°.
Pelargonic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_8H_{17})O\\O\\\mathbf{C}(C_8H_{17})O\end{matrix}\right.$			+5°.	—
Palmitic anhydride	$\left\{\begin{matrix}\mathbf{C}(C_{15}H_{31})O\\O\\\mathbf{C}(C_{15}H_{31})O\end{matrix}\right.$			53·°8.	—

2. *ANHYDRIDES OF THE DIHYDRIC MONOBASIC ACIDS.*

Formation.—By applying heat to a dihydric monobasic acid, thus :—

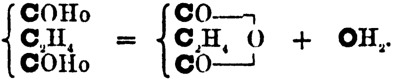
$$\underset{\text{Lactic acid.}}{\left\{\begin{matrix}\mathbf{C}MeHHo\\\mathbf{C}OHo\end{matrix}\right.} = \underset{\substack{\text{Lactide.}\\\text{(Lactic anhydride.)}}}{\left\{\begin{matrix}\mathbf{C}MeH\\\mathbf{C}O\end{matrix}\right.O} + \underset{\text{Water.}}{OH_2}.$$

Reaction.—Boiled with water, and especially with alkalies, they reproduce the acids from which they were derived :—

$$\underset{\text{Lactide.}}{\left\{\begin{matrix}\mathbf{C}MeH\\\mathbf{C}O\end{matrix}\right.O} + \underset{\text{Water.}}{OH_2} = \underset{\text{Lactic acid.}}{\left\{\begin{matrix}\mathbf{C}MeHHo\\\mathbf{C}OHo.\end{matrix}\right.}$$

3. *ANHYDRIDES OF THE DIHYDRIC DIBASIC ACIDS.*

Formation.—By the action of heat, or of substances having a strong affinity for water, upon the dihydric dibasic acids:—



$$\left\{\begin{array}{l}\mathbf{C}\text{OHo}\\ \mathbf{C}_2\text{H}_4\\ \mathbf{C}\text{OHo}\end{array}\right. = \left\{\begin{array}{l}\mathbf{C}\text{O}-\!\!\urcorner\\ \mathbf{C}_2\text{H}_4\ \ \text{O}\\ \mathbf{C}\text{O}-\!\!\lrcorner\end{array}\right. + \mathbf{O}\text{H}_2.$$

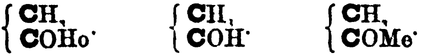
Succinic acid. Succinic anhydride. Water.

Reaction.—Like the anhydrides of the first and second classes, they unite with water, reproducing the acids from which they were derived.

CHAPTER XXVI.

THE KETONES.

The ketones are derived from the fatty acids by the substitution of the hydroxyl of the latter by a monad positive radical; they thus resemble the aldehydes in constitution:—



$$\left\{\begin{array}{l}\mathbf{C}\text{H}_3\\ \mathbf{C}\text{OHo}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\text{H}_3\\ \mathbf{C}\text{OH}\end{array}\right. \qquad \left\{\begin{array}{l}\mathbf{C}\text{H}_3\\ \mathbf{C}\text{OMe}\end{array}\right.$$

Acetic acid. Acetic aldehyde. Acetone.

The ketones may also be correctly described as compounds of carbonic oxide with monad positive radicals, thus:—

$$\mathbf{C}\text{OMe}_2.$$

Acetone.

By the action of nascent hydrogen upon the ketones, they are converted into secondary alcohols, whilst the aldehydes, under the same treatment, yield normal alcohols :—

$$\underset{\text{Acetone.}}{\left\{\begin{matrix}CH_3\\COMe\end{matrix}\right.} + H_2 = \underset{\text{Isopropylic alcohol.}}{\left\{\begin{matrix}CH_3\\CMeHHo\end{matrix}\right.}$$

Ketones, unlike aldehydes, do not oxidize spontaneously; neither do they reduce ammoniacal solution of argentic oxide.

Like aldehydes, many of them combine with hydric potassic or hydric sodic sulphite.

Formation.—1. By the action of the zinc compounds of the positive monad radicals upon chloracids :—

$$2\underset{\text{Chloracid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COCl\end{matrix}\right.} + \underset{\text{Zinc compound.}}{Zn(C_nH_{2n+1})_2} = 2\underset{\text{Ketone.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CO(C_nH_{2n+1})\end{matrix}\right.} + \underset{\text{Zincic chloride.}}{ZnCl_2}.$$

2. By the action of sodic ethide and its homologues on carbonic oxide :—

$$\underset{\text{Carbonic oxide.}}{CO} + \underset{\text{Sodium compound.}}{2Na(C_nH_{2n+1})} = \underset{\text{Ketone}}{\left\{\begin{matrix}C_nH_{2n+1}\\CO(C_nH_{2n+1})\end{matrix}\right.} + Na_2.$$

3. By the distillation of the salts of the fatty acids :—

$$2\underset{\text{Potassic salt of fatty acid.}}{\left\{\begin{matrix}C_nH_{2n+1}\\COKo\end{matrix}\right.} = \underset{\text{Ketone.}}{\left\{\begin{matrix}C_nH_{2n+1}\\CO(C_nH_{2n+1})\end{matrix}\right.} + \underset{\text{Potassic carbonate}}{COKo_2}.$$

4. By distilling together salts of two different fatty acids, ketones containing two different positive radicals are obtained :—

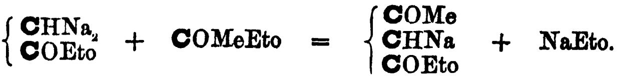
$$\underset{\text{Potassic butyrate.}}{\left\{\begin{matrix}CEtH_2\\COKo\end{matrix}\right.} + \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.} = \underset{\text{Propylmethyl ketone.}}{\left\{\begin{matrix}CEtH_2\\COMe\end{matrix}\right.} + \underset{\text{Potassic carbonate.}}{COKo_2}.$$

5. Numerous ketones may also be produced by the following series of reactions.

By the action of sodium upon ethylic acetate hydrogen becomes replaced by sodium :—

$$\underset{\text{Ethylic acetate.}}{\left\{\begin{matrix}CH_3\\COEto\end{matrix}\right.} + Na_2 = \underset{\text{Ethylic disodacetate.}}{\left\{\begin{matrix}CHNa_2\\COEto\end{matrix}\right.} + H_2.$$

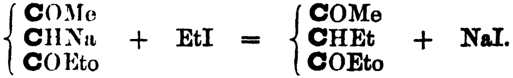
The ethylic disodacetate is acted upon by excess of ethylic acetate as follows:—



$$\left\{\begin{array}{l}\mathrm{CHNa_2}\\ \mathrm{COEto}\end{array}\right. + \mathrm{COMeEto} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CHNa}\\ \mathrm{COEto}\end{array}\right. + \mathrm{NaEto}.$$

Ethylic disodacetate. Ethylic acetate. Ethylic sodaceto-acetate. Sodic ethylate.

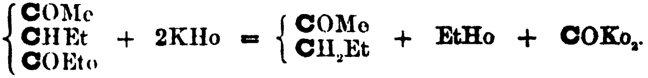
When ethylic iodide is added to ethylic sodaceto-acetate the following reaction occurs:—



$$\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CHNa}\\ \mathrm{COEto}\end{array}\right. + \mathrm{EtI} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CHEt}\\ \mathrm{COEto}\end{array}\right. + \mathrm{NaI}.$$

Ethylic sodaceto-acetate. Ethylic iodide. Ethylic ethaceto-acetate.

Lastly, ebullition of ethylic ethaceto-acetate with potassic hydrate converts it into ethylated acetone, alcohol, and potassic carbonate:—



$$\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CHEt}\\ \mathrm{COEto}\end{array}\right. + \mathrm{2KHo} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CH_2Et}\end{array}\right. + \mathrm{EtHo} + \mathrm{COKo_2}.$$

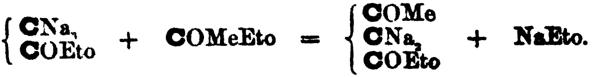
Ethylic ethaceto-acetate. Potassic hydrate. Ethylated acetone. Alcohol. Potassic carbonate.

Ethylated acetone is obviously acetone in which one atom of hydrogen has been replaced by ethyl.

A second atom of hydrogen in acetone may be replaced in the following analogous series of reactions:—

$$2\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COEto}\end{array}\right. + \mathrm{3Na_2} = 2\left\{\begin{array}{l}\mathrm{CNa_3}\\ \mathrm{COEto}\end{array}\right. + \mathrm{3H_2}.$$

Ethylic acetate. Ethylic trisodacetate.



$$\left\{\begin{array}{l}\mathrm{CNa_3}\\ \mathrm{COEto}\end{array}\right. + \mathrm{COMeEto} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CNa_2}\\ \mathrm{COEto}\end{array}\right. + \mathrm{NaEto}.$$

Ethylic trisodacetate. Ethylic acetate. Ethylic disodaceto-acetate. Sodic ethylate.

$$\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CNa_2}\\ \mathrm{COEto}\end{array}\right. + \mathrm{2EtI} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CEt_2}\\ \mathrm{COEto}\end{array}\right. + \mathrm{2NaI}.$$

Ethylic disodaceto-acetate. Ethylic iodide. Ethylic diethaceto-acetate.

$$\left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CEt_2}\\ \mathrm{COEto}\end{array}\right. + 2\mathrm{KHo} = \left\{\begin{array}{l}\mathrm{COMe}\\ \mathrm{CEt_2H}\end{array}\right. + \mathrm{EtHo} + \mathrm{COKo_2}.$$

Ethylic diethaceto-acetate. Potassic hydrate. Diethylated acetone. Alcohol. Potassic carbonate.

6. By the action of zincic ethide on the chlorides obtained from the dibasic acids, ketones containing dyad radicals are produced; thus :—

Succinylic chloride submitted to the action of zincic ethide gives ethylene diethylic ketone :—

$$\left\{\begin{array}{l}\mathrm{COCl}\\ (\mathrm{C_2H_4})''\\ \mathrm{COCl}\end{array}\right. + \mathrm{ZnEt_2} = \left\{\begin{array}{l}\mathrm{COEt}\\ (\mathrm{C_2H_4})''\\ \mathrm{COEt}\end{array}\right. + \mathrm{ZnCl_2}.$$

Succinylic chloride. Zincic ethide. Ethylene diethylic ketone. Zincic chloride.

The following is a list of the names, constitutional formulæ, and boiling-points of those ketones which are best known :—

			Boiling-point.
	Acetone	$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COMe}\end{array}\right.$	56°.
	Methylated acetone. (*Ethyl acetyl, methyl acetone.*)	$\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COMe}\end{array}\right.$	81°.
Isomeric.	Dimethylated acetone. (*Ethyl acetone.*)	$\left\{\begin{array}{l}\mathrm{CMe_2H}\\ \mathrm{COMe}\end{array}\right.$	93°·5
	Ethylated acetone	$\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{COMe}\end{array}\right.$	101°.
	Propione. (*Ethyl propionyl.*)	$\left\{\begin{array}{l}\mathrm{CMeH_2}\\ \mathrm{COEt}\end{array}\right.$	101°.
Isomeric.	Methyl valeral	$\left\{\begin{array}{l}\mathrm{CPrH_2}\\ \mathrm{COMe}\end{array}\right.$	120°.
	Ethyl butyral	$\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{COEt}\end{array}\right.$	128°.
Isomeric.	Diethylated acetone	$\left\{\begin{array}{l}\mathrm{CEt_2H}\\ \mathrm{COMe}\end{array}\right.$	138°.
	Butyrone	$\left\{\begin{array}{l}\mathrm{CEtH_2}\\ \mathrm{COPr}\end{array}\right.$	144°.

Little is known of the ketones of the C_nH_{2n-7} series. The following have been obtained :—

Benzophenone $\left(\left\{\begin{matrix}C_6H_5\\CO(C_6H_5)\end{matrix}\right.\right)$, the ketone of benzoic acid, is obtained by heating potassic benzoate.

Methyl benzole or *methyl benzoyl* $\left(\left\{\begin{matrix}CH_3\\CO(C_6H_5)\end{matrix}\right.\right)$ is prepared by distilling together calcic acetate and benzoate.

Phthalylic chloride, treated with zincic ethide, produces *phenylene diethylic ketone* :—

$$\begin{array}{ccccccc} \left\{\begin{matrix}COCl\\(C_6H_4)''\\COCl\end{matrix}\right. & + & ZnEt_2 & = & \left\{\begin{matrix}COEt\\(C_6H_4)''\\COEt\end{matrix}\right. & + & ZnCl_2. \\ \text{Phthalylic chloride.} & & \text{Zincic ethide.} & & \text{Phenylene diethylic ketone.} & & \text{Zincic chloride.} \end{array}$$

CHAPTER XXVII.

ETHEREAL SALTS.

THESE compounds correspond to the metallic oxysalts of the acids.

The acids from which they are derived may be either mineral or organic; but the base must always be organic. The haloid ethereal salts are excluded from this family; they have been already described as haloid ethers.

The ethereal salts are produced by reactions analogous to those employed for the preparation of metallic salts :—

$$\begin{array}{ccccccc} \left\{\begin{matrix}CH_3\\COHo\end{matrix}\right. & + & KHo & = & \left\{\begin{matrix}CH_3\\COKo\end{matrix}\right. & + & OH_2. \\ \text{Acetic acid.} & & \text{Potassic hydrate.} & & \text{Potassic acetate.} & & \text{Water.} \end{array}$$

$$\begin{array}{ccccccc} \left\{\begin{matrix}CH_3\\COHo\end{matrix}\right. & + & EtHo & = & \left\{\begin{matrix}CH_3\\COEto\end{matrix}\right. & + & OH_2. \\ \text{Acetic acid.} & & \text{Ethylic hydrate.} & & \text{Ethylic acetate.} & & \text{Water.} \end{array}$$

But as the hydrates of the organic radicals do not act upon acids so energetically as potassic hydrate, it is often advisable to employ the acid in the form of a potassic salt, and the radical as a sulphoacid; thus, with acids of the acetic series:—

$$\underset{\text{Sulphoacid.}}{SO_2Ho(C_nH_{2n+1}O)} + \underset{\text{Potassic salt.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ COKo \end{matrix}\right.} = \underset{\text{Ethereal salt.}}{\left\{\begin{matrix} C_nH_{2n+1} \\ CO(C_nH_{2n+1}O) \end{matrix}\right.} + \underset{\text{Hydric potassic sulphate.}}{SO_2HoKo.}$$

Monobasic acids form only one ethereal salt with each monohydric alcohol; and this salt is always normal.

With dihydric alcohols they each form two ethereal salts, and with trihydric alcohols three ethereal salts. These are also normal. Thus with acetic acid we have:—

Acetic salt of a monohydric alcohol:—

$$\underset{\text{Ethylic acetate.}}{\left\{\begin{matrix} CH_3 \\ COEto \end{matrix}\right.}\cdot$$

Acetic salts of a dihydric alcohol:—

$$\underset{\text{Monacetic glycol.}}{\left\{\begin{matrix} CH_2Ho \\ CH_2\text{-}O\text{-}CMeO \end{matrix}\right.}\cdot \qquad \underset{\text{Diacetic glycol}}{\left\{\begin{matrix} CH_2\text{-}O\text{-}CMeO \\ CH_2\text{-}O\text{-}CMeO \end{matrix}\right.}\cdot$$

Acetic salts of a trihydric alcohol:—

$$\underset{\text{Monacetin.}}{\left\{\begin{matrix} CH_2Ho \\ CHHo \\ CH_2\text{-}O\text{-}CMeO \end{matrix}\right.}. \qquad \underset{\text{Diacetin.}}{\left\{\begin{matrix} CH_2\text{-}O\text{-}CMeO \\ CHHo \\ CH_2\text{-}O\text{-}CMeO \end{matrix}\right.}. \qquad \underset{\text{Triacetin.}}{\left\{\begin{matrix} CH_2\text{-}O\text{-}CMeO \\ CH\text{-}O\text{-}CMeO. \\ CH_2\text{-}O\text{-}CMeO \end{matrix}\right.}$$

Dibasic acids form, with monohydric alcohols, two series of ethereal salts:—

1. Acid ethereal salts, as:—

Succinethylic acid .... $\left\{\begin{matrix} COEto \\ C_2H_4 \\ COHo \end{matrix}\right..$

2. Normal ethereal salts, as:—

Ethylic succinate .... $\left\{\begin{matrix} COEto \\ C_2H_4 \\ COEto \end{matrix}\right..$

In the same manner, tribasic acids form with monohydric alcohols three series of ethereal salts, the first two of which are acid, and the third normal.

Prolonged contact with water generally decomposes ethereal salts, liberating the radicals of the bases in the form of alcohols:—

$$\underset{\substack{\text{Methylic}\\\text{sulphomethylate.}}}{\mathbf{S}O_2Meo_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{\mathbf{S}O_2Ho_2} + \underset{\substack{\text{Methylic}\\\text{alcohol.}}}{2MeHo.}$$

Ebullition with potassic hydrate, especially when the latter is dissolved in alcohol, effects this transformation very speedily:—

$$\underset{\substack{\text{Ethylic}\\\text{acetate.}}}{\left\{\begin{matrix}\mathbf{C}H_3\\\mathbf{C}OEto\end{matrix}\right.} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Potassic}\\\text{acetate.}}}{\left\{\begin{matrix}\mathbf{C}H_3\\\mathbf{C}OKo\end{matrix}\right.} + \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{EtHo.}$$

CHAPTER XXVIII.

ORGANIC COMPOUNDS CONTAINING TRIAD AND PENTAD NITROGEN OR THEIR ANALOGUES.

THIS numerous family may be divided into two great classes:—

1. Compounds of triad nitrogen, phosphorus, arsenic, antimony, and bismuth.

2. Compounds of pentad nitrogen, phosphorus, arsenic, antimony, and bismuth.

I. *COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES.*

This class may be again subdivided as follows:—

Positive.	Neutral.	Negative.
1. Amines.	1. Amides.	1. Imides and nitrides of negative radicals.
2. Phosphines.	2. Alkalamides.	
3. Arsines.	3. Trichlorinated and tribrominated amines.	
4. Stibines.	4. Haloid compounds of oxybases.	
5. Bismuthines.		
6. Oxybases.		

Of these the Amines and Amides are the most important.

Positive Section.

1. *THE AMINES.*

The Amines are commonly termed organic bases or artificial alkaloids; they are divided into—

A. Monamines.
B. Diamines.
C. Triamines.
D. Tetramines.

The tetramines have been but little investigated.

A. *MONAMINES.*

There are three kinds of monamines:—

α. Primary monamines.
β. Secondary monamines.
γ. Tertiary monamines.

α. *Primary Monamines.*

	General formulæ.
Methyl or C_nH_{2n+1} series	$\mathbf{N}(C_nH_{2n+1})H_2$.
Vinyl or C_nH_{2n-1} series	$\mathbf{N}(C_nH_{2n-1})H_2$.
Phenyl or C_nH_{2n-7} series	$\mathbf{N}(C_nH_{2n-7})H_2$.

Formation.—1. By the reduction of the nitro-substitution compounds of the hydrides of the positive radicals by sulphuretted hydrogen, ammonic sulphide, zinc and sulphuric acid, or iron and acetic acid:—

$$\underset{\text{Nitrobenzol.}}{\mathbf{N}(C_6H_5)O_2} + \underset{\text{Sulphuretted hydrogen.}}{3SH_2} = \underset{\text{Aniline.}}{\mathbf{N}(C_6H_5)H_2} + \underset{\text{Water.}}{2OH_2} + S_3.$$

2. By treating cyanic ethers with boiling solution of potassic

hydrate. The reaction is perfectly analogous to the decomposition of cyanic acid with potassic hydrate:—

$$\begin{array}{ccccccc} \mathbf{C}\mathrm{N''Ho} & + & 2\mathrm{KHo} & = & \mathbf{C}\mathrm{OKo_2} & + & \mathbf{N}\mathrm{H_3}. \\ \text{Cyanic acid.} & & \text{Potassic hydrate.} & & \text{Potassic carbonate.} & & \text{Ammonia.} \end{array}$$

$$\begin{array}{ccccccc} \mathbf{C}\mathrm{N'''Eto} & + & 2\mathrm{KHo} & = & \mathbf{C}\mathrm{OKo_2} & + & \mathbf{N}\mathrm{EtH_2}. \\ \text{Ethylic cyanate.} & & \text{Potassic hydrate.} & & \text{Potassic carbonate.} & & \text{Ethylamine.} \end{array}$$

3. By the action of the haloid compounds of the monad positive radicals upon ammonia, and subsequent action of potassic hydrate upon the product so formed:—

$$\begin{array}{ccccc} \mathbf{N}\mathrm{H_3} & + & \mathrm{EtI} & = & \mathbf{N}\mathrm{EtH_3I}. \\ \text{Ammonia.} & & \text{Ethylic iodide.} & & \text{Ethylammonic iodide.} \end{array}$$

$$\begin{array}{ccccccccc} \mathbf{N}\mathrm{EtH_3I} & + & \mathrm{KHo} & = & \mathbf{N}\mathrm{EtH_2} & + & \mathrm{KI} & + & \mathbf{O}\mathrm{H_2}. \\ \text{Ethylammonic iodide.} & & \text{Potassic hydrate.} & & \text{Ethylamine.} & & \text{Potassic iodide.} & & \text{Water.} \end{array}$$

The following are a few of the primary monamines:—

Methylamine............ $\mathbf{N}\mathrm{MeH_2}$ or $\mathbf{N}\mathrm{(CH_3)H_2}$.
Ethylamine .... $\mathbf{N}\mathrm{EtH_2}$ or $\mathbf{N}\mathrm{(C_2H_5)H_2}$.
Butylamine ... . $\mathbf{N}\mathrm{BuH_2}$ or $\mathbf{N}\mathrm{(C_4H_9)H_2}$.
Amylamine .... $\mathbf{N}\mathrm{AyH_2}$ or $\mathbf{N}\mathrm{(C_5H_{11})H_2}$.
Allylamine...... . ..... $\mathbf{N}\mathrm{AllH_2}$ or $\mathbf{N}\mathrm{(C_3H_5)H_2}$.
Phenylamine (*Aniline*) $\mathbf{N}\mathrm{PhH_2}$ or $\mathbf{N}\mathrm{(C_6H_5)H_2}$.
Tolylamine (*Toluidine*) $\mathbf{N}\mathrm{ToH_2}$ or $\mathbf{N}\mathrm{(C_6H_4Me)H_2}$.

Reactions.—Treated with nitrous acid, they evolve nitrogen and yield the corresponding alcohols:—

$$\begin{array}{ccccccccc} \mathbf{N}\mathrm{PhH_2} & + & \mathbf{N}\mathrm{OHo} & = & \mathrm{PhHo} & + & \mathrm{N_2} & + & \mathbf{O}\mathrm{H_2}. \\ \text{Phenylamine.} & & \text{Nitrous acid.} & & \text{Phenylic alcohol.} & & & & \text{Water.} \end{array}$$

β. *Secondary Monamines.*

	General formulæ.
Methyl or C_nH_{2n+1} series	$\mathbf{N}(C_nH_{2n+1})_2H$.
Vinyl or C_nH_{2n-1} series............	$\mathbf{N}(C_nH_{2n-1})_2H$.
Phenyl or C_nH_{2n-7} series	$\mathbf{N}(C_nH_{2n-7})_2H$.

The secondary monamines are derived from ammonia by the replacement of two atoms of hydrogen by monad positive radicals. They are sometimes called *Imidogen bases.*

Formation.—By the action of the haloid compounds of the monad positive radicals on the primary monamines, and subsequent treatment with potassic hydrate:—

$$\underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Diethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_2H_2I.}$$

$$\underset{\substack{\text{Diethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_2H_2I} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\text{Diethylamine.}}{\mathbf{N}Et_2H} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{KI} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

By using the iodide of a radical different from that already contained in the primary monamine, secondary monamines may be formed containing two different radicals, thus:—

$$\underset{\substack{\text{Phenylamine.}\\\text{(Aniline.)}}}{\mathbf{N}PhH_2} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Ethylphenylammonic}\\\text{iodide.}}}{\mathbf{N}EtPhH_2I.}$$

$$\underset{\substack{\text{Ethylphenylam-}\\\text{monic iodide.}}}{\mathbf{N}EtPhH_2I} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{KHo} = \underset{\substack{\text{Ethylphenylamine.}\\\text{(Ethylaniline.)}}}{\mathbf{N}EtPhH} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{KI} + \underset{\text{Water}}{\mathbf{O}H_2.}$$

The following secondary monamines are known:—

Dimethylamine	$\mathbf{N}Me_2H$	or $\mathbf{N}(CH_3)_2H.$
Diethylamine	$\mathbf{N}Et_2H$	or $\mathbf{N}(C_2H_5)_2H.$
Methylethylamine	$\mathbf{N}MeEtH$	or $\mathbf{N}(CH_3)(C_2H_5)H.$
Dibutylamine	$\mathbf{N}Bu_2H$	or $\mathbf{N}(C_4H_9)_2H.$
Ethylamylamine	$\mathbf{N}EtAyH$	or $\mathbf{N}(C_2H_5)(C_5H_{11})H.$
Ethylphenylamine	$\mathbf{N}EtPhH$	or $\mathbf{N}(C_2H_5)(C_6H_5)H.$
Piperidine		$\mathbf{N}(C_5H_{10})''H.$
Conine		$\mathbf{N}(C_8H_{14})''H.$

γ. *Tertiary Monamines.*

Formation.—1. By acting upon the secondary monamines with the iodides of the monad positive radicals, and subsequently treating the product with potassic hydrate:—

$$\underset{\text{Diethylamine.}}{\mathbf{N}Et_2H} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI} = \underset{\substack{\text{Triethylammonic}\\\text{iodide.}}}{\mathbf{N}Et_3HI.}$$

$\mathbf{N}Et_3HI$	+	KHo	=	$\mathbf{N}Et_3$	+	KI	+	OH_2.
Triethylammonic iodide.		Potassic hydrate.		Triethylamine.		Potassic iodide.		Water.

By varying the radicals, tertiary monamines with several different radicals may be formed. The following are a few of the known tertiary monamines:—

Trimethylamine	$\mathbf{N}Me_3$	or	$\mathbf{N}(CH_3)_3$.
Triethylamine	$\mathbf{N}Et_3$	or	$\mathbf{N}(C_2H_5)_3$.
Tributylamine	$\mathbf{N}Bu_3$	or	$\mathbf{N}(C_4H_9)_3$.
Triamylamine	$\mathbf{N}Ay_3$	or	$\mathbf{N}(C_5H_{11})_3$.
Methyl-ethyl-phenylamine	$\mathbf{N}MeEtPh$	or	$\mathbf{N}(CH_3)(C_2H_5)(C_6H_5)$.
Pyridine			$\mathbf{N}(C_5H_5)'''$.
Picoline			$\mathbf{N}(C_6H_7)'''$.
Lutidine			$\mathbf{N}(C_7H_9)'''$.
Collidine			$\mathbf{N}(C_8H_{11})'''$.
Parvoline			$\mathbf{N}(C_9H_{13})'''$.

The constitution of the triad radicals contained in the last five bases is not known.

2. When phenylammonic chloride (aniline hydrochlorate) and methylic alcohol are digested together at from 280° to 300°, the non-phenylic hydrogen becomes replaced by methyl, thus:—

$\mathbf{N}PhH_3Cl$	+	$MeHo$	=	$\mathbf{N}PhMeH_2Cl$	+	OH_2.
Phenylammonic chloride.		Methylic alcohol.		Methylphenylammonic chloride.		
$\mathbf{N}PhMeH_2Cl$	+	$MeHo$	=	$\mathbf{N}PhMe_2HCl$	+	OH_2.
Methylphenylammonic chloride.		Methylic alcohol.		Dimethylphenylammonic chloride.		

By continuing the digestion longer, the phenylic hydrogen is also replaced by methyl according to the following reaction:—

$\mathbf{N}(C_6H_4)Me_2HCl$	+	$MeHo$	=	$\mathbf{N}(C_6H_4Me)Me_2HCl$	+	OH_2.
Dimethylphenylammonic chloride.		Methylic alcohol.		Dimethyltolylammonic chloride.		

By these reactions the following tertiary monamines have been produced:—

Dimethylaniline	$\mathbf{N}(C_6H_5)Me_2$.
Dimethyltoluidine	$\mathbf{N}(C_6H_4Me)Me_2$.
Dimethylxylidine	$\mathbf{N}(C_6H_3Me_2)Me_2$.
Dimethylcumidine	$\mathbf{N}(C_6H_2Me_3)Me_2$.
Dimethylcymidine	$\mathbf{N}(C_6HMe_4)Me_2$.

The final product which may be expected to result from this reaction, $\mathbf{N}(C_6Me_5)Me_2$, has not yet been obtained.

Tertiary monamines, when acted upon by the iodides of monad positive radicals, yield iodides which are not decomposed by potassic hydrate. In this manner tertiary monamines may be distinguished from primary and secondary monamines. The three may be distinguished from each other by the alternate action of ethylic iodide and potassic hydrate: thus, as we have just seen, tertiary monamines are recognized by producing immediately iodides which are not decomposed by potassic hydrate; a secondary monamine, however, produces an iodide decomposable by potassic hydrate; but the base thus liberated is tertiary, and will therefore be transformed immediately into the stable iodide by a second application of ethylic iodide. A primary monamine requires three applications of ethylic iodide and potassic hydrate to produce the same result.

B. *DIAMINES.*

Formation.—The diamines are formed by coupling together two atoms of nitrogen in two molecules of ammonia, or of a primary or secondary monamine, by a dyad radical, which at the same time takes the place of two atoms of hydrogen; thus:—

$$\left\{\begin{matrix}\mathbf{N}H_2\\ Et''\\ \mathbf{N}H_2\end{matrix}\right. . \qquad \left\{\begin{matrix}\mathbf{N}H\\ Et''\\ \mathbf{N}H\end{matrix}\right. . \qquad \left\{\begin{matrix}\mathbf{N}\\ Et''\\ \mathbf{N}\end{matrix}\right. , \text{ or } \left\{\begin{matrix}\mathbf{N}Et''\\ Et''\\ \mathbf{N}Et''\end{matrix}\right. .$$

Primary diamine. Secondary diamine. Tertiary diamine.

This reaction is effected by treating ammonia or a primary or secondary monamine with the haloid salt (preferably a bromide) of the dyad radical, thus:—

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Ethylenic dibromide.}}{Et''Br_2} = \underset{\text{Ethylene-diammonic dibromide.}}{\left\{\begin{matrix}NH_3Br\\Et''\\NH_3Br\end{matrix}\right.}.$$

When the salts of ethylene diammonium are decomposed by potassic hydrate, an oxide of the compound nitrogenous radical is produced, thus:—

$$\underset{\text{Ethylene-diammonic dibromide.}}{\left\{\begin{matrix}NH_3Br\\Et''\\NH_3Br\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Ethylene-diammonic oxide.}}{\left\{\begin{matrix}NH_3\urcorner\\Et''\;\;O\\NH_3\lrcorner\end{matrix}\right.} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic bromide.}}{2KBr}.$$

In this respect most of the diamines differ from the monamines.

Urea and its derivatives belong to the class of diamines.

These compounds are produced by boiling a solution of ammonic cyanate or ethylammonic cyanate, or a homologue of the latter. In these compounds, the two atoms of nitrogen are held together by the dyad radical carbonyl, CO:—

$$\underset{\text{Ammonic cyanate.}}{CN'''(N^{v}H_4O)} = \underset{\text{Urea.}}{\left\{\begin{matrix}NH_2\\CO\\NH_2\end{matrix}\right.}.$$

$$\underset{\text{Ethyl-ammonic cyanate.}}{CN'''(N^{v}EtH_3O)} = \underset{\text{Ethyl urea.}}{\left\{\begin{matrix}NHEt\\CO\\NH_2\end{matrix}\right.}.$$

By heating ammonic carbonate to 130°–140° in closed vessels for a few hours, urea is produced:—

$$\underset{\text{Ammonic carbonate.}}{CO(NH\ O)_2} = \underset{\text{Urea.}}{\left\{\begin{matrix}NH_2\\CO\\NH_2\end{matrix}\right.} + \underset{\text{Water.}}{2OH_2}.$$

Ureas in which ethyl and other monad positive radicals are substituted for hydrogen may also be obtained by the action of ammonia or a monamine on the cyanic ethers, thus:—

$$\mathrm{CN'''Eto} + \mathrm{NH_3} = \left\{\begin{array}{l}\mathrm{NHEt}\\ \mathrm{CO}\\ \mathrm{NH_2}\end{array}\right. .$$

Ethylic cyanate. Ammonia. Ethyl urea.

$$\mathrm{CN'''Eto} + \mathrm{NH_2Et} = \left\{\begin{array}{l}\mathrm{NHEt}\\ \mathrm{CO}\\ \mathrm{NHEt}\end{array}\right. .$$

Ethylic cyanate. Ethylamine. Diethyl urea.

Reaction.—Urea is decomposed by nitrous anhydride:—

$$\left\{\begin{array}{l}\mathrm{NH_2}\\ \mathrm{CO}\\ \mathrm{NH_2}\end{array}\right. + \mathrm{N_2O_3} = \mathrm{CO_2} + 2\mathrm{N_2} + 2\mathrm{OH_2}.$$

Urea. Nitrous anhydride. Carbonic anhydride. Water.

The following is a list of the best-known diamines:—

Ethylene diamine .... $\left\{\begin{array}{l}\mathrm{NH_2}\\ \mathrm{Et''}\\ \mathrm{NH_2}\end{array}\right.$.

Ethylene diethyl diamine .... $\left\{\begin{array}{l}\mathrm{NHEt}\\ \mathrm{Et''}\\ \mathrm{NHEt}\end{array}\right.$.

Urea .... $\left\{\begin{array}{l}\mathrm{NH_2}\\ \mathrm{CO}\\ \mathrm{NH_2}\end{array}\right.$.

Sulphur urea .... $\left\{\begin{array}{l}\mathrm{NH_2}\\ \mathrm{CS''}\\ \mathrm{NH_2}\end{array}\right.$.

Ethyl urea .... $\left\{\begin{array}{l}\mathrm{NHEt}\\ \mathrm{CO}\\ \mathrm{NH_2}\end{array}\right.$

Sulphophenylurea.................... $\left\{\begin{array}{l}\mathrm{NHPh}\\ \mathrm{CS''}\\ \mathrm{NH_2}\end{array}\right.$.

C. *TRIAMINES.*

To this class of organic bases belong many of the aniline colours and their derivatives. ***Mauveine*** was the first discovered of these bodies; it is obtained by the action of concentrated sulphuric acid and red potassic chromate upon aniline. It is also produced by heating the coloured product obtained by the action of a solution of bleaching powder upon aniline. The molecular formula of mauveine is

$$N_4C_{26}H_{24}.$$

It is probably a tetramine with the constitution shown in the following formula:—

$$N_4(C_7H_6)''_2(C_6H_4)''_2H_4.$$

Rosaniline is obtained from a mixture of aniline and toluidine by the action of various reagents, such as carbonic chloride, stannic chloride, mercuric chloride, ferric chloride, cupric chloride, the sulphuric and nitric salts of tin and mercury, and, lastly, arsenic acid which has superseded all other reagents for the technical preparation of the salts of this base.

By the replacement of hydrogen in rosaniline by positive radicals, other bases, forming with acids valuable colouring-matters, are produced.

The following is a list of the best-known of these bases:—

Rosaniline, the base of magenta	$N_3(C_6H_4)''(C_7H_6)''_2H_3$.
Phenyl rosaniline, the base of dahline	$N_3(C_6H_4)''(C_7H_6)''_2PhH_2$.
Diphenyl rosaniline, the base of aniline violet	$N_3(C_6H_4)''(C_7H_6)''_2Ph_2H$.
Triphenyl rosaniline, the base of aniline blue	$N_3(C_6H_4)''(C_7H_6)''_2Ph_3$.
Tritolyl rosaniline, the base of toluidine blue	$N_3(C_6H_4)''(C_7H_6)''_2(C_7H_7)_3$.

Triethyl rosaniline, the base of Hofmann's violet	$\mathbf{N}_3(C_6H_4)''(C_7H_6)''_2Et_3$.
Chrysaniline, Nicholson's yellow	$N_3C_{20}H_{17}$.
Leukaniline	$N_3C_{20}H_{21}$.

Rosaniline appears to be formed by the abstraction of three molecules of hydrogen from one molecule of aniline and two molecules of toluidine, thus :—

$$\underset{\text{Aniline.}}{\mathbf{N}(C_6H_5)H_2} + \underset{\text{Toluidine.}}{2\mathbf{N}(C_7H_7)H_2} - 3H_2 = \underset{\text{Rosaniline.}}{\mathbf{N}_3(C_6H_4)''(C_7H_6)''_2H_3}.$$

The phenyl derivatives of rosaniline are produced as salts of hydrochloric acid by heating rosaniline hydrochlorate with various proportions of aniline, thus :—

$$\underset{\text{Rosaniline hydrochlorate.}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2H_4Cl} + \underset{\text{Aniline.}}{\mathbf{N}PhH_2} =$$

$$\underset{\text{Phenyl-rosaniline hydrochlorate}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2PhH_3Cl} + \underset{\text{Ammonia}}{\mathbf{N}H_3}.$$

$$\underset{\text{Rosaniline hydrochlorate.}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2H_4Cl} + \underset{\text{Aniline.}}{2\mathbf{N}PhH_2} =$$

$$\underset{\text{Diphenyl-rosaniline hydrochlorate.}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2Ph_2H_2Cl} + \underset{\text{Ammonia}}{2\mathbf{N}H_3}.$$

$$\underset{\text{Rosaniline hydrochlorate.}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2H_4Cl} + \underset{\text{Aniline.}}{3\mathbf{N}PhH_2} =$$

$$\underset{\text{Triphenyl-rosaniline hydrochlorate.}}{{}^{iv}(\mathbf{N}_3)^{xi}(C_6H_4)''(C_7H_6)''_2Ph_3HCl} + \underset{\text{Ammonia.}}{3\mathbf{N}H_3}.$$

The salts of tritolyl rosaniline are formed by analogous reactions.

Triethyl rosaniline is obtained by heating to 100°, in a close vessel, rosaniline with ethylic iodide dissolved in alcohol:—

$$\underset{\text{Rosaniline.}}{\mathbf{N}_3(C_6H_4)''(C_7H_6)''_2H_3} + \underset{\text{Ethylic iodide.}}{3EtI} = \underset{\text{Triethyl rosaniline.}}{\mathbf{N}_3(C_6H_4)''(C_7H_6)''_2Et_3} + \underset{\text{Hydriodic acid.}}{3HI.}$$

Trimethyl and triamyl rosaniline are obtained by analogous processes.

Chrysaniline is formed as a secondary product in the manufacture of rosaniline.

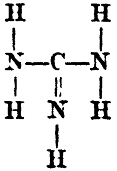
Leukaniline is produced by the action of zinc upon an acid solution of rosaniline:—

$$\underset{\text{Rosaniline.}}{\mathbf{N}_3C_{20}H_{19}} + H_2 = \underset{\text{Leukaniline.}}{N_3C_{20}H_{21}.}$$

OTHER AMINES.

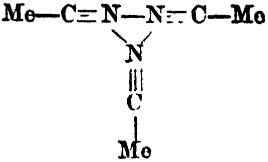
Subjoined are the names and formulæ of a number of organic bases which cannot at present be satisfactorily classified:—

Guanine	$C_5H_5N_5O$.
Guanidine	$\mathbf{C}(NH)''(NH_2)(NH_2)$ or $\mathbf{C}(NH)''Ad_2$.

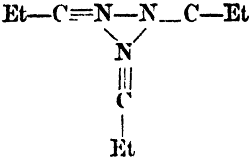


Furfurine	$C_{15}H_{12}N_2O_3$.
Amarine	$C_{21}H_{18}N_2$.
Thialdine	$C_6H_{13}NS_2$.
Dibutyraldine	$C_8H_{17}NO$.
Acridine	$C_{24}H_{18}N_2$.

Cyanmethine ... ${}^{vi}(\mathbf{N}_3)^{ix}(CMe)'''_3$ ...



Cyanethine .. ... ${}^{vi}(\mathbf{N}_3)^{ix}(CEt)'''_3$ ...



THE NATURAL ALKALOIDS.

Of the constitution of these organic bases very little is known. The following is a list of the chief of them, with the sources whence they are derived:—

Alkaloids from Opium.

Hydrocotarnine	$C_{12}H_{15}NO_3$.
Morphine	$C_{17}H_{19}NO_3$.
Codeine	$C_{18}H_{21}NO_3$, $\mathbf{OH_2}$.
Thebaine	$C_{19}H_{21}NO_3$.
Protopine	$C_{20}H_{19}NO_5$.
Papaverine	$C_{20}H_{21}NO_4$.
Cryptopine	$C_{21}H_{23}NO_5$.
Laudanosine	$C_{21}H_{27}NO_4$.
Narcotine	$C_{22}H_{23}NO_7$.
Narceine	$C_{23}H_{29}NO_9$.

From Cinchona Bark.

Quinine	$C_{20}H_{24}N_2O_2$.
Cinchonine	$C_{20}H_{24}N_2O$.
Aricine	$C_{23}H_{26}N_2O_4$.

From Nightshade.

Atropine	$C_{17}H_{23}NO_3$.

From Tobacco.

Nicotine	$C_{10}H_{14}N_2$.

From Nux vomica.

Strychnine	$C_{21}H_{22}N_2O_2$.
Brucine	$C_{23}H_{26}N_2O_4$.

From Tea, Coffee, and Cocoa.

Theobromine	$C_7H_8N_4O_2$.
Caffeine (*Theine*)	$C_8H_{10}N_4O_2$.

2, 3, 4. *THE PHOSPHINES, ARSINES, STIBINES, AND BISMUTHINES.*

The bases containing phosphorus may be obtained, like the amines, by the displacement of hydrogen in phosphuretted hydrogen. The tertiary compounds only of arsenic, antimony, and bismuth are known; and they are produced by reactions of which the following may be regarded as a type:—

$$\underset{\text{Sodic arsenide.}}{AsNa_3} + \underset{\text{Ethylic iodide.}}{3EtI} = \underset{\text{Triethyl arsine.}}{AsEt_3} + \underset{\text{Sodic iodide.}}{3NaI}.$$

Primary and secondary phosphines are obtained by the action of methylic or ethylic iodide and zincic oxide upon phosphonic iodide. With ethylic iodide the following reactions occur:—

$$\underset{\text{Phosphonic iodide.}}{2PH_4I} + \underset{\text{Ethylic iodide.}}{2EtI} + ZnO = \underset{\text{Ethyl-phosphonic iodide.}}{2PEtH_3I} + ZnI_2 + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Phosphonic iodide.}}{2PH_4I} + \underset{\text{Ethylic iodide.}}{4EtI} + 3ZnO = \underset{\text{Diethyl-phosphonic zincic iodide.}}{2PEt_2H(ZnI)I} + \underset{\text{Water.}}{3OH_2} + ZnI_2.$$

These reactions take place side by side; but the primary and secondary phosphines are readily separated from each other by the consecutive action of water and alkalies upon the products of the above operation.

The addition of water to the mixed product liberates the primary phosphine from its compound, whilst the compound of the secondary phosphine resists even boiling water, but easily decomposes under the influence of alkalies.

The tertiary phosphines are produced by the action of the zinc compounds of the monad positive radicals upon phosphorous chloride:—

$$\underset{\text{Zincic ethide.}}{3\mathbf{Zn}Et_2} + \underset{\text{Phosphorous chloride.}}{2\mathbf{P}Cl_3} = \underset{\text{Triethyl phosphine.}}{2\mathbf{P}Et_3} + \underset{\text{Zincic chloride.}}{3\mathbf{Zn}Cl_2}.$$

They may also be obtained in combination with hydriodic acid by the action of phosphonic iodide upon the alcohols:—

$$\underset{\text{Phosphonic iodide.}}{\mathbf{P}H_4I} + \underset{\text{Ethylic alcohol.}}{3EtHo} = \underset{\text{Triethyl-phosphonic iodide.}}{\mathbf{P}Et_3HI} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

By the action of alkalies upon triethyl-phosphonic iodide triethyl phosphine is liberated:—

$$\underset{\text{Triethyl-phosphonic iodide.}}{\mathbf{P}Et_3HI} + KHo = \underset{\text{Triethyl-phosphine.}}{\mathbf{P}Et_3} + KI + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The following Table contains the names of the known phosphines, arsines, and stibines:—

Primary Phosphines.

	Formula.	Boiling-point.
Methyl phosphine	$\mathbf{P}MeH_2$.........	−14°.
Ethyl phosphine	$\mathbf{P}EtH_2$	25°.

Secondary Phosphines.

Dimethyl phosphine	$\mathbf{P}Me_2H$.........	25°.
Diethyl phosphine	$\mathbf{P}Et_2H$	85°.

Tertiary Phosphines.

	Formula.	Boiling-point.
Trimethyl phosphine	$\mathbf{P}Me_3$	41°.
Triethyl phosphine	$\mathbf{P}Et_3$	127°·5.

Tertiary Arsines.

Trimethyl arsine	$\mathbf{As}Me_3$	120°.
Triethyl arsine	$\mathbf{As}Et_3$	140°.

Tertiary Stibines.

Trimethyl stibine	$\mathbf{Sb}Me_3$	——
Triethyl stibine	$\mathbf{Sb}Et_3$	158°.
Triamyl stibine	$\mathbf{Sb}Ay_3$	——

Tertiary Bismuthine.

Triethyl bismuthine	$\mathbf{Bi}Et_3$	——

Character.—The phosphines, arsines, stibines, and bismuthines possess very energetic affinities for negative elements. Many of them are spontaneously inflammable in air and oxygen. Most, probably all, unite with an atom of oxygen or a molecule of chlorine, bromine, or iodine, forming compounds in which the grouping element becomes pentadic. Thus, by the absorption of oxygen, triethyl-phosphine is transformed into phosphoric triethoxide:—

$$\underset{\text{Triethyl-phosphine.}}{\mathbf{P}Et_3} + O = \underset{\text{Phosphoric triethoxide.}}{\mathbf{P}Et_3O}$$

5. *OXYBASES.*

These compounds are only known in the arsenic series.

Arsenious oxybases.

Only one of these, cacodylic oxide, has been carefully investigated.

By the distillation of potassic acetate with arsenious anhydride, a compound known as cacodyl, $'\mathbf{As}''_2Me_4$, is produced. This substance may also be prepared by the action of methylic iodide upon an alloy of sodium and arsenic containing $'\mathbf{As}''_2Na_4$:—

$$\underset{\text{Sodic arsenide.}}{'\mathbf{As}''_2Na_4} + \underset{\text{Methylic iodide.}}{4MeI} = \underset{\text{Cacodyl.}}{'\mathbf{As}''_2Me_4} + \underset{\text{Sodic iodide.}}{4NaI.}$$

By allowing cacodyl to absorb oxygen slowly, an oily liquid containing cacodylic oxide ($\mathbf{As}_2Me_4O$) is formed.

This oxybase does not appear to unite with oxygen acids, but it is attacked by hydrochloric acid, forming cacodylic chloride:—

$$\underset{\text{Cacodylic oxide.}}{\left\{\begin{matrix}\mathbf{As}Me_2\\ O\\ \mathbf{As}Me_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Cacodylic chloride.}}{2\mathbf{As}Me_2Cl} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

Cacodylic oxide, when exposed to moist air, absorbs water and oxygen, forming cacodylic acid:—

$$\underset{\text{Cacodylic oxide.}}{\mathbf{As}_2Me_4O} + O_2 + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Cacodylic acid.}}{2\mathbf{As}Me_2OHo.}$$

CHAPTER XXIX.

ORGANIC COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES (continued).

NEUTRAL SECTION.

1. *THE AMIDES.*

These compounds are formed by the substitution of amidogen (NH_2) for the oxatylic hydroxyl of organic acids. They are most conveniently written on the diadelphic type, but may also be formulated upon the ammonia type.

If the acid contain only one semimolecule of oxatyl, a monamide is the result; if two semimolecules of oxatyl are present in the acid, a diamide is generally formed, &c. Secondary and tertiary compounds can also be produced, as in the case of the amines; but they belong to the negative section of this family.

A. *MONAMIDES.*

I. *Primary Monamides.*

Acetamide :—

$$\left\{\begin{matrix}\mathbf{C}\mathrm{MeO}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right. \text{ or } \mathbf{N}\mathrm{H}_2(\mathrm{CMeO}), \text{ or } \left\{\begin{matrix}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OAd}\end{matrix}\right.\cdot$$

Chloracetamide :—

$$\left\{\begin{matrix}\mathbf{C}(\mathrm{CH}_2\mathrm{Cl})\mathrm{O}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right. \text{ or } \mathbf{N}\mathrm{H}_2[\mathbf{C}(\mathrm{CH}_2\mathrm{Cl})\mathrm{O}], \text{ or } \left\{\begin{matrix}\mathbf{C}\mathrm{H}_2\mathrm{Cl}\\ \mathbf{C}\mathrm{OAd}\end{matrix}\right.\cdot$$

Benzamide :—

$$\left\{\begin{matrix}\mathbf{C}(\mathrm{C}_6\mathrm{H}_5)\mathrm{O}\\ \mathbf{N}\mathrm{H}_2\end{matrix}\right. \text{ or } \mathbf{N}\mathrm{H}_2[\mathbf{C}(\mathrm{C}_6\mathrm{H}_5)\mathrm{O}], \text{ or } \left\{\begin{matrix}\mathbf{C}_6\mathrm{H}_5\\ \mathbf{C}\mathrm{OAd}\end{matrix}\right.\cdot$$

Formation.—1. By the distillation of the ammonic salts of the monobasic acids :—

$$\underset{\text{Ammonic acetate.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{O}(\mathrm{N^vH_4O})\end{matrix}\right.} = \underset{\text{Acetamide.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{O}(\mathrm{N'''H_2})\end{matrix}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

2. By the action of ammonia upon the chloracids :—

$$\underset{\text{Acetylic chloride.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{OCl}\end{matrix}\right.} + \underset{\text{Ammonia.}}{\mathbf{N}\mathrm{H}_3} = \underset{\text{Acetamide.}}{\left\{\begin{matrix}\mathbf{C}\mathrm{H}_3\\ \mathbf{C}\mathrm{O}(\mathrm{N'''H_2})\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}}.$$

3. By the action of ammonia on the ethereal salts of the monobasic acids:—

$$\underset{\text{Ethylic acetate.}}{\left\{\begin{matrix}CH_3\\COEto\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Acetamide.}}{\left\{\begin{matrix}CH_3\\CO(N'''H_2)\end{matrix}\right.} + \underset{\text{Alcohol.}}{EtHo.}$$

Reactions.—1. Boiled with aqueous solutions of acids, the primary monamides yield ammonic salts and acids:—

$$\underset{\text{Acetamide.}}{\left\{\begin{matrix}CH_3\\CO(N'''H_2)\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{OH_2} = \underset{\text{Ammonic chloride.}}{NH_4Cl} + \underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.}\cdot$$

2. Boiled with potassic hydrate, ammonia is evolved, and a potassic salt, corresponding to the amide, is formed.

$$\underset{\text{Acetamide.}}{\left\{\begin{matrix}CH_3\\CO(N'''H_2)\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Potassic acetate.}}{\left\{\begin{matrix}CH_3\\COKo\end{matrix}\right.}\cdot$$

II. *Secondary Monamides.*

$$\text{Diacetimide} \ldots\ N(CMeO)_2H \quad \text{or} \left\{\begin{matrix}CH_3\\CO\\NH\\CO\\CH_3\end{matrix}\right. .$$

$$\text{Succinimide} \ldots\ldots\ NH\left[\left\{\begin{matrix}CO\\C_2H_4\\CO\end{matrix}\right.\right]'' \quad \text{or} \left\{\begin{matrix}CO\\Et''\\CO\end{matrix}\right. (N''H)''.$$

These bodies possess a negative character, and are treated of under the negative section of this class as *imides of negative radicals* (p. 210).

Tertiary monamides are little known. They are the *nitrides of negative radicals* (see p. 210).

B. *DIAMIDES.*

The diamides may be regarded as derived from two molecules of ammonia, by the substitution of a dyad negative radical for

two atoms of hydrogen; or they may be considered to be formed by the substitution of amidogen for the hydroxyl contained in the two semimolecules of oxatyl in dibasic acids:—

Primary Diamides.

Oxamide ... $\left\{\begin{matrix}\mathbf{N}H_2\\(C_2O_2)''\\\mathbf{N}H_2\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{C}OAd\\\mathbf{C}OAd\end{matrix}\right.$.

Succinamide .. $\mathbf{N}_2H_4(C_4H_4O_2)''$ or $\mathbf{N}_2H_4\left[\left\{\begin{matrix}\mathbf{C}O\\Et''\\\mathbf{C}O\end{matrix}\right.\right]''$, or $\left\{\begin{matrix}\mathbf{C}OAd\\Et''\\\mathbf{C}OAd\end{matrix}\right.$.

Formation.—1. By the action of heat upon the normal ammonic salts of dibasic acids:—

$$\underset{\text{Ammonic oxalate.}}{\left\{\begin{matrix}\mathbf{C}O(N^vH_4O)\\\mathbf{C}O(N^vH_4O)\end{matrix}\right.} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\\mathbf{C}O(N'''H_2)\end{matrix}\right.} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

2. By the action of ammonia on the ethereal salts of dibasic acids:—

$$\underset{\text{Ethylic oxalate.}}{\left\{\begin{matrix}\mathbf{C}OEto\\\mathbf{C}OEto\end{matrix}\right.} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3} = \underset{\text{Oxamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\\mathbf{C}O(N'''H_2)\end{matrix}\right.} + \underset{\text{Alcohol.}}{2EtHo}.$$

3. By the action of ammonia on the chloro-dibasic acids:—

$$\underset{\text{Ammonia.}}{4\mathbf{N}H_3} + \underset{\text{Succinylic chloride.}}{\left\{\begin{matrix}\mathbf{C}OCl\\Et''\\\mathbf{C}OCl\end{matrix}\right.} = \underset{\text{Succinamide.}}{\left\{\begin{matrix}\mathbf{C}O(N'''H_2)\\Et''\\\mathbf{C}O(N'''H_2)\end{matrix}\right.} + \underset{\text{Ammonic chloride.}}{2\mathbf{N}H_4Cl}.$$

The *secondary* and *tertiary diamides* are but little known.

C. *TRIAMIDES.*

Primary Triamides.—The primary triamides may be regarded as derived from tribasic acids by the substitution of amidogen for the hydroxyl contained in the three semimolecules of oxatyl of these acids, or as derived from three molecules of ammonia by the replacement of three atoms of hydrogen by the residue of a tribasic acid. A good example of a triamide is

$$\text{Citramide} \ldots\ldots \begin{cases} \mathbf{C}\mathrm{HHo(COAd)} \\ \mathbf{C}\mathrm{H(COAd)} \\ \mathbf{C}\mathrm{H_2(COAd)} \end{cases} \quad \text{or } \mathbf{N}_3\mathrm{H}_6(\mathrm{C}_6\mathrm{H}_5\mathrm{O}_4)'''.$$

Citramide is formed by the action of ammonia on ethylic citrate.

Secondary and *tertiary triamides* have not yet been formed.

2. *THE ALKALAMIDES.*

These compounds occupy an intermediate position between the amines and the amides. They are derived from ammonia by the substitution of part of the hydrogen by positive, and part by negative radicals; and inasmuch as two atoms at least of hydrogen must be so substituted, no primary alkalamide can exist.

Secondary and tertiary monalkalamides, dialkalamides, and trialkalamides are known.

Ethyl acetamide	$\mathbf{N}\mathrm{HEt(CMeO)}$.
Ethyl diacetamide	$\mathbf{N}\mathrm{Et(CMeO)_2}$.
Diethyl oxamide	$\mathbf{N}_2\mathrm{H_2Et_2(C_2O_2)''}$.
Diphenyl-carbonyl-oxalyl diamide	$\mathbf{N}_2\mathrm{(C_6H_5)_2(CO)''(C_2O_2)''}$.
Citryl-triphenyl-triamide	$\mathbf{N}_3\mathrm{H_3(C_6H_5)_3(C_6H_5O_4)'''}$.

The alkalamides incline towards a positive character, their degree of alkalinity being about equal to that of urea.

3. *THE TRICHLORINATED AND TRIBROMINATED AMINES.*

If the hydrogen in an amine be gradually substituted by chlorine or bromine, the basic character of the amine gradually diminishes, and finally a neutral compound is obtained.

This reaction has been studied in the case of aniline, which loses basic energy by the successive replacement of two atoms of hydrogen, and finally becomes neutral by the substitution of three atoms of chlorine or bromine for three of hydrogen:—

$$\underset{\text{Aniline.}}{\mathbf{N}H_2(C_6H_5).}\quad \underset{\text{Chloraniline.}}{\mathbf{N}H_2(C_6H_4Cl).}\quad \underset{\text{Dichloraniline.}}{\mathbf{N}H_2(C_6H_3Cl_2).}\quad \underset{\text{Trichloraniline.}}{\mathbf{N}H_2(C_6H_2Cl_3).}$$

4. *THE HALOID COMPOUNDS OF OXYBASES.*

These bodies are only known in the arsenic series; they are formed by the action of chlorine, bromine, or iodine upon cacodyl and its homologues, or of hydrochloric acid, hydrobromic acid, or hydriodic acid upon the oxybases.

General formula... $\mathbf{As}(C_nH_{2n+1})_2Cl.$

NEGATIVE SECTION.

THE IMIDES AND NITRIDES.

$$\text{General formula} \;..\; \begin{cases} \text{of imides ..} & \mathbf{N}H(C_nH_{2n-1}O)_2, \\ \text{of nitrides .} & \mathbf{N}(C_nH_{2n-1}O)_3. \end{cases}$$

Formation.—By the action of chloracids (the so-called chlorides of negative radicals) upon amides:—

$$\underset{\text{Acetamide.}}{\mathbf{N}H_2(CMeO)} + \underset{\substack{\text{Acetylic}\\\text{chloride.}}}{\mathbf{C}MeOCl} = \underset{\text{Diacetimide.}}{\mathbf{N}H(CMeO)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

A repetition of this reaction gives acetylic nitride, which may also be obtained by heating a mixture of acetonitrile and acetic anhydride to 200°.

An imide may also be formed by the substitution of a dyad negative radical for two atoms of hydrogen in ammonia, thus:—

Succinimide......... $\mathbf{N}H(C_4H_4O_2)''$, or $\mathbf{N}H\left[\left\{\begin{matrix}\mathbf{C}O\\ Et''\\ \mathbf{C}O\end{matrix}\right.\right]''.$

These bodies have hitherto received but little attention.

CHAPTER XXX.

II. *COMPOUNDS OF PENTAD NITROGEN AND OF ITS ANALOGUES.*

This class of compounds contains the following series :—

Positive.	*Neutral.*	*Negative.*
1. Caustic Nitrogen bases.	1. Salts of Amines.	1. Organic arsenic acids, oxychlorides, and chlorides.
2. „ Phosphorus bases.	2. „ Phosphines.	
3. „ Arsenic bases.	3. „ Arsines.	
4. „ Antimony bases.	4. „ Stibines.	
5. Oxyarsenic bases.	5. „ Oxyarsenic bases.	2. Organic antimonic acids.
6. Oxyantimonic bases.	6. „ Oxyantimonic bases.	

POSITIVE COMPOUNDS.

1. *Caustic Nitrogen Bases.*—

General formula...... $\mathbf{N}(C_nH_{2n+1})_4Ho$.

In each positive radical *n* must be a positive integer. The radicals need not be all of the same atomic weight.

Formation.—By the action of argentic hydrate upon the iodides of the compound ammoniums :—

$$\underset{\text{Tetrethylammonic iodide.}}{\mathbf{N}Et_4I} + \underset{\text{Argentic hydrate.}}{AgHo} = \underset{\text{Tetrethylammonic hydrate.}}{\mathbf{N}Et_4Ho} + \underset{\text{Argentic iodide.}}{AgI.}$$

2. *Caustic Phosphorus Bases.*

3. *Caustic Arsenic Bases.*

4. *Caustic Antimony Bases.*—

By displacing the **N** in the above general formula and in the equation by **P**, **As**, and **Sb**, the constitution and formation of these three series of compounds will be expressed.

5. *Oxyarsenic Bases.*—These bodies, which are diacid bases, are obtained by the slow oxidation of the tertiary monarsines :—

$$\underset{\text{Tertiary monarsine.}}{\mathbf{As}(C_nH_{2n+1})_3} + O = \underset{\text{Oxyarsenic base.}}{\mathbf{As}(C_nH_{2n+1})_3O.}$$

6. *Oxyantimonic Bases.*—These are formed in a manner exactly analogous to that in which the oxyarsenic bases are produced.

NEUTRAL COMPOUNDS.

1. *Salts of Amines.*

General formulæ:—

$$\mathbf{N}(C_nH_{2n+1})(C_mH_{2m+1})_3Cl.$$
$$\mathbf{N}_2(C_nH_{2n})''(C_mH_{2m})''_2H_2Cl_2.$$
$$\mathbf{N}_3(C_nH_{2n-1})'''(C_mH_{2m-1})'''_2H_3Cl_3.$$

In the first formula m may $=0$; in the second, C_mH_{2m} may be displaced by H_2; and in the third, C_mH_{2m-1} may be substituted by H_3.

Formation.—Like the analogous compounds of ammonia, the salts of the amines are formed by the direct union of acids with the amines without elimination of water, thus:—

$$\underset{\text{Ethylamine.}}{\mathbf{N}EtH_2} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethylammonic chloride.}}{\mathbf{N}EtH_3Cl.}$$

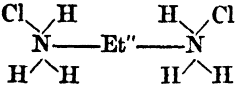
The haloid salts of the amines may also be produced by the union of the haloid ethers of the monad positive radicals with the amines (for reaction see p. 192).

Character.—The salts of the diamines and triamines are often found to contain only one molecule of acid, instead of two or three as shown in the above general formulæ, which indicate the composition of the normal salts. The nitrogen atoms are in such cases united together by one of the bonds of each, besides being linked by the polyad radicals, thus:—

$$\mathbf{N}^{v}{}_2(C_nH_{2n})''(C_mH_{2m})''_2H(NO_3);$$
$${}^{iv}(\mathbf{N}_3)^{xi}(C_nH_{2n-1})'''(C_mH_{2m-1})'''_2HCl.$$

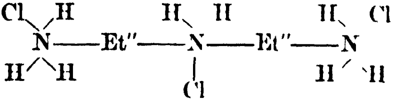
The difference between these two classes of salts will be rendered more evident by a comparison of the following graphic and symbolic formulæ:—

Normal Salts.



or $\mathbf{N}_2H_6Et''Cl_2$, or $\left\{\begin{array}{l}\mathbf{N}H_3Cl\\ Et''\\ \mathbf{N}H_3Cl\end{array}\right.$.

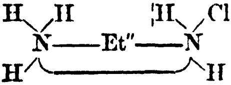
Ethylene-diammonic dichloride.



Diethylene-triammonic trichloride

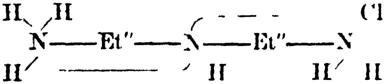
or $\mathbf{N}_3H_8Et''_2Cl_3$ or $\left\{\begin{array}{l}\mathbf{N}H_3Cl\\ Et''\\ \mathbf{N}H_2Cl.\\ Et''\\ \mathbf{N}H_3Cl\end{array}\right.$

Monacid Salts.



or $'\mathbf{N}^{iv}_2H_5Et''Cl$ or $\left\{\begin{array}{l}\mathbf{N}H_2\\ \mathbf{N}H_2Cl\end{array}\right.Et''$.

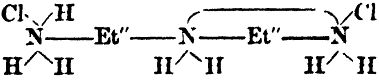
Ethylene-diammonic monochloride



Diethylene-triammonic monochloride

or $^{iv}(\mathbf{N}_3)^{xi}H_6Et''_2Cl$ or $\left\{\begin{array}{l}\mathbf{N}H_2\\ \mathbf{N}H\\ \mathbf{N}H_2Cl\end{array}\right.\begin{array}{l}Et''\\ Et''.\end{array}$

Diacid Salt.



Diethylene-triammonic dichloride.

or $''(\mathbf{N}_3)^{xiii}H_7Et''_2Cl_2$ or $\left\{\begin{array}{l}\mathbf{N}H_3Cl\\ \mathbf{N}H_2\\ \mathbf{N}H_2Cl\end{array}\right.\begin{array}{l}Et''\\ Et''.\end{array}$

2. *Salts of Phosphines.*

3. *Salts of Arsines.*

4. *Salts of Stibines.*

These three series of salts all present close analogies with the salts of the amines both in constitution and in the mode of their formation. The mode of formation of several of them is shown at pages 202 and 203.

5. *Salts of Oxyarsenic Bases.*

$$\mathbf{As}(C_nH_{2n+1})_3Cl_2.$$

Formation.—By the action of acids on the oxyarsenic bases:

$$\underset{\text{Arsenic trimethoxide.}}{\mathbf{As}Me_3O} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Arsenic trimethodichloride.}}{\mathbf{As}Me_3Cl_2} + \underset{\text{Water.}}{OH_2}$$

6. *Salts of Oxyantimonic Bases.*

These resemble the previous salts in formation and constitution.

NEGATIVE COMPOUNDS.

1. *Organic Arsenic Acids, Oxychlorides, and Chlorides.*

The following are the principal bodies of this class:—

Monomethylarsenic acid...........	$\mathbf{As}MeOHo_2$.
Arsenic oxydichlormethide.........	$\mathbf{As}MeOCl_2$.
Arsenic tetrachlormethide	$\mathbf{As}MeCl_4$
Cacodylic acid	$\mathbf{As}Me_2OHo$.
Cacodylic trichloride	$\mathbf{As}Me_2Cl_3$.

2. *Organic Antimonic Acids.*

No exploration of this series has yet been made. The members of it will doubtless be found to have close analogies with the corresponding series of arsenic compounds.

CHAPTER XXXI.

ORGANO-BORON AND SILICON COMPOUNDS

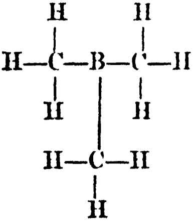
This family is divided into the two following classes:—

1. Organo-boron compounds.
2. Organo-silicon compounds.

1. *Organo-boron compounds.*

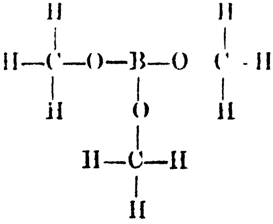
These compounds contain boron directly united with the carbon of monad positive radicals, and are thus distinguished from organic compounds containing boron, as seen in the following formulæ:—

Organo-boron compound.



Boric methide.

Organic compound containing boron



Methylic borate.

The organo-boron compounds are produced by the replacement of methoxyl or ethoxyl in methylic or ethylic borate by monad positive radicals. Hitherto only the radicals methyl and ethyl have been thus combined with boron.

BORIC METHIDE.

$\mathbf{B}(CH_3)_3$, or $\mathbf{B}Me_3$.

Molecular weight = 56. *Molecular volume* $\square\square$. 1 *litre of boric methide gas weighs* 28 *criths. Condenses at* 10° *under a pressure of four atmospheres.*

Preparation.—By adding to ethylic borate an ethereal solution of zincic methide, when boric methide is evolved as gas:—

$$\underset{\substack{\text{Ethylic}\\\text{borate.}}}{2\mathbf{B}Eto_3} + \underset{\substack{\text{Zincic}\\\text{methide.}}}{3\mathbf{Zn}Me_2} = \underset{\substack{\text{Boric}\\\text{methide.}}}{2\mathbf{B}Me_3} + \underset{\substack{\text{Zincic}\\\text{ethylate.}}}{3\mathbf{Zn}Eto_2}.$$

Reactions.—1. Inflames spontaneously in air or oxygen.

2. Combines energetically with ammonia, forming ammonia-boric methide:—

$$\underset{\text{Ammonia.}}{\mathbf{N}H_3} + \underset{\substack{\text{Boric}\\\text{methide.}}}{\mathbf{B}Me_3} = \underset{\substack{\text{Ammonia-boric}\\\text{methide.}}}{\mathbf{N}H_3,\mathbf{B}Me_3}.$$

3. Boric methide combines readily with potash, soda, lime, and baryta, forming compounds the composition of which is not known with certainty.

AMMONIA-BORIC METHIDE.

$\mathbf{N}H_3,\mathbf{B}Me_3$.

Molecular weight = 73. *Molecular volume* (*anomalous*) $\boxplus$. *Fuses at* 56°. *Boils at* 110°. 1 *litre of ammonia-boric methide vapour weighs* 18·25 *criths.*

Formed as above described.

Reactions.—1. Cupric chloride absorbs ammonia from the vapour of ammonia-boric methide, reducing the volume of the vapour to one half and leaving boric methide gas:—

$$\underset{\substack{\text{Ammonia-boric}\\\text{methide.}}}{6(\mathbf{N}H_3,\mathbf{B}Me_3)} + 2CuCl_2 = \underset{\substack{\text{Ammonia-cupric}\\\text{chloride.}}}{2\mathbf{Cu}Cl_2,6\mathbf{N}H_3} + \underset{\substack{\text{Boric}\\\text{methide.}}}{6\mathbf{B}Me_3}.$$

2. Ammonia-boric methide is readily decomposed by acids; even carbonic acid decomposes it. With hydrochloric acid the reaction is:—

$$\underset{\substack{\text{Ammonia-boric}\\\text{methide.}}}{\mathbf{N}H_3,\mathbf{B}Me_3} + HCl = \underset{\substack{\text{Ammonic}\\\text{chloride.}}}{\mathbf{N}H_4Cl} + \underset{\substack{\text{Boric}\\\text{methide.}}}{\mathbf{B}Me_3}.$$

BORIC ETHIDE.

$\mathbf{B}(C_2H_5)_3$ or $\mathbf{B}Et_3$.

Molecular weight =98. *Molecular volume* □□. 1 *litre of boric ethide vapour weighs* 49 *criths. Boils at* 95° C. *Sp. gr. of liquid* ·6961 *at* 23°.

Preparation.—By the action of zincic ethide upon ethylic borate:—

$$\underset{\substack{\text{Ethylic}\\\text{borate.}}}{2\mathbf{B}Eto_3} + \underset{\substack{\text{Zincic}\\\text{ethide.}}}{3\mathbf{Zn}Et_2} = \underset{\substack{\text{Boric}\\\text{ethide.}}}{2\mathbf{B}Et_3} + \underset{\substack{\text{Zincic}\\\text{ethylate.}}}{3\mathbf{Zn}Eto_2}.$$

Reactions.—1. Inflames spontaneously in air, and explodes in oxygen.

2. Allowed to oxidize gradually, boric ethide forms boric etho-diethylate:—

$$\mathbf{B}Et_3 + O_2 = \mathbf{B}EtEto_2.$$

3. Heated with hydrochloric acid to 99°, it slowly evolves ethylic hydride, and is converted into boric dietho-chloride:—

$$\underset{\substack{\text{Boric}\\\text{ethide.}}}{\mathbf{B}Et_3} + HCl = \underset{\substack{\text{Boric dietho-}\\\text{chloride.}}}{\mathbf{B}Et_2Cl} + \underset{\substack{\text{Ethylic}\\\text{hydride.}}}{EtH}.$$

4. Boric ethide combines very energetically with ammoniacal gas, forming ammonia-boric ethide:—

$$\underset{\text{Ammonia.}}{\mathbf{N}H_3} + \underset{\substack{\text{Boric}\\\text{ethide.}}}{\mathbf{B}Et_3} = \underset{\substack{\text{Ammonia-boric}\\\text{ethide.}}}{\mathbf{N}H_3,\mathbf{B}Et_3}.$$

BORIC ETHO-DIETHYLATE.

$\mathbf{B}EtEto_2$.

Boils at 125° C.

Preparation.—By the slow action of oxygen upon boric ethide as above described.

Reaction.—In contact with water it is instantly decomposed, forming *boric etho-dihydrate* :—

$$\underset{\text{Boric etho-diethylate.}}{\mathbf{B}EtEto_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Boric etho-dihydrate.}}{\mathbf{B}EtHo_2} + \underset{\text{Alcohol.}}{2HEto.}$$

AMMONIA-BORIC ETHIDE.

$\mathbf{N}H_3,\mathbf{B}Et_3$.

Formed by the union of ammonia gas with boric ethide as above described.

Reaction.—Decomposed by acids but not by carbonic acid. With hydrochloric acid the reaction is as follows:—

$$\underset{\text{Ammonia-boric ethide.}}{\mathbf{N}H_3,\mathbf{B}Et_3} + HCl = \underset{\text{Ammonic chloride.}}{\mathbf{N}H_4Cl} + \underset{\text{Boric ethide.}}{\mathbf{B}Et_3.}$$

2. *Organo-silicon compounds.*

The great similarity in chemical functions between carbon and silicon seems to justify the anticipation that a great number of compounds of silicon will be produced analogous in constitution to the organic compounds of carbon. Already several such compounds are known, as for instance:—

Silico-compounds.	Organic analogues.
$\mathbf{Si}H_4$. Silicic hydride.	$\mathbf{C}H_4$. Marsh gas.
$\mathbf{Si}HCl_3$. Silicon chloroform.	$\mathbf{C}HCl_3$. Chloroform.
$\left\{\begin{matrix}\mathbf{Si}HO\\ O\\ \mathbf{Si}HO\end{matrix}\right. .$ Silicoformic anhydride.	$\left\{\begin{matrix}\mathbf{C}HO\\ O\\ \mathbf{C}HO\end{matrix}\right. .$ Unknown formic anhydride.

Following the analogy of organic compounds, the substitution of one of the atoms of hydrogen in silicic hydride by the hitherto unknown radical silicon methyl ($\mathbf{Si}H_3$) would yield a body constituted like the molecule of methyl or ethylic hydride,

$$\left\{\begin{matrix}\mathbf{Si}H_3\\ \mathbf{Si}H_3\end{matrix}\right..$$

From this, silicoethylic chloride ($\mathbf{Si}_2H_5Cl$) ought to be obtained; and then, by the substitution of hydroxyl for chlorine, the silicon-analogue of common alcohol ($\mathbf{Si}_2H_5Ho$). None of these compounds containing silicon directly combined with silicon have hitherto been formed; indeed, unlike the tetrad elements, carbon, tin, and titanium, silicon appears to have little tendency to form such compounds. Amongst the host of silicon minerals there is not one in which the assumption of the existence of silicon combined directly with silicon is admissible. Disilicic hexachloride ($\mathbf{Si}_2Cl_6$) has, however, been recently formed.

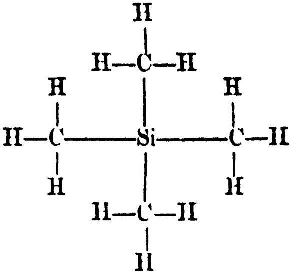
But, although these true silicon analogues of the more complex organic compounds have not hitherto been obtained, yet a large number of bodies which contain silicon atoms directly combined with carbon have been synthetically produced; and many of these substances exhibit interesting analogies with corresponding compounds containing carbon in the place of silicon. These are the bodies which are included in the class of *organo-silicon compounds.* The following Table contains the names and constitutional formulæ of the chief members of this class, together with those of their derivatives, such as ethylic silicate ($\mathbf{Si}Eto_4$), which do not, strictly speaking, belong to it, inasmuch as they no longer contain silicon directly combined with carbon:—

Name.	Formula.	Boiling-point.
Silicic methide	$\mathbf{Si}Me_4$	30°·5
Disilicic oxy-hexamethylate	$\left\{\begin{matrix}\mathbf{Si}Meo_3\\ O\\ \mathbf{Si}Meo_3\end{matrix}\right.$	202

Name.	Formula.	Boiling-point. °
Silicic methylate	$SiMeo_4$	121
Silicic ethide	$SiEt_4$	152·5
Silicic dimethylate ethylate	$SiMeo_2Eto_2$	145
Silicic chlortriethylate	$SiClEto_3$	156
Silicic dichlorethylate	$SiCl_2Eto_2$	—
Silicic ethylate	$SiEto_4$	166·5
Silicic triethylate amylate	$SiEto_3Ayo$	220
Disilicic oxy-hexaethylate	$\left\{\begin{array}{l} SiEto_3 \\ O \\ SiEto_3 \end{array}\right.$	235
Disilicic oxy-hexaethide	$\left\{\begin{array}{l} SiEt_3 \\ O \\ SiEt_3 \end{array}\right.$	227
Silicic hydrotriethylate	$SiHEto_3$	134
Silicic ethotriethylate	$SiEtEto_3$	158·5
Silicic dieth-ethylate	$SiEt_2Eto_2$	155·5
Silicic trieth-ethylate	$SiEt_3Eto$	153
Silicic dietho-chlorethylate	$SiEt_2ClEto$	148
Silicic chlortriethide	$SiEt_3Cl$	143·5
Silicic dichlorethide	$SiEt_2Cl_2$	129
Silicic trichlorethide	$SiEtCl_3$	—
Silicic diethoxide	$SiEt_2O$	—
Siliconylic chloride	$\left\{\begin{array}{l} SiEt_3 \\ CMeHCl \end{array}\right.$	185
Siliconylic alcohol	$\left\{\begin{array}{l} SiEt_3 \\ CMeHHo \end{array}\right.$	190
Siliconylic acetate	$\left\{\begin{array}{l} CH_3 \\ CO(SiC_8H_{19}O) \end{array}\right.$	211
Silicic aceto-triethylate	$\left\{\begin{array}{l} SiEto_3 \\ O \\ COM \end{array}\right.$	—
Silicic acetylate	$Si(COMe)_4$	—
Silicopropionic acid	$\left\{\begin{array}{l} CMeH_2 \\ SiOHo \end{array}\right.$	—
Silicic triethohydrate (*Triethylsilicol*)	$SiEt_3Ho$	158·5

SILICIC METHIDE.

$\mathbf{Si}(CH_3)_4$
or
$\mathbf{Si}Me_4$.



Molecular weight =88·5. *Molecular volume* ☐☐. 1 *litre of silicic methide vapour weighs* 44·25 *criths. Boils at* 30°·5.

Formation.—By the action of zincic methide upon silicic chloride at a temperature of from 120° to 200°.

$$\underset{\text{Silicic chloride.}}{\mathbf{Si}Cl_4} + \underset{\text{Zincic methide.}}{2\mathbf{Zn}Me_2} = \underset{\text{Silicic methide.}}{\mathbf{Si}Me_4} + \underset{\text{Zincic chloride.}}{2\mathbf{Zn}Cl_2}.$$

SILICIC ETHIDE.

$\mathbf{Si}Et_4$.

Molecular weight =144·5. *Molecular volume* ☐☐. 1 *litre of silicic ethide vapour weighs* 72·25 *criths. Boils at* 152°·5.

Preparation.—By the substitution of zincic ethide for zincic methide in the reaction last described, silicic ethide is produced.

Reactions.—Treated with chlorine, one atom of hydrogen is replaced by an atom of chlorine, and *siliconylic chloride* is formed:—

$$\underset{\text{Silicic ethide.}}{\mathbf{Si}Et_3(CMeH_2)} + Cl_2 = \underset{\text{Siliconylic chloride.}}{\left\{\begin{matrix}\mathbf{Si}Et_3\\ \mathbf{C}MeHCl\end{matrix}\right.} + HCl.$$

At the same time a portion of the silicic ethide is converted into dichlorinated silicic ethide, which, when heated with aqueous alcohol and potassic acetate, yields disilicic oxyethide,

$$\left\{\begin{array}{l}\mathbf{Si}Et_3\\ O\\ \mathbf{Si}Et_3\end{array}\right. .$$

SILICIC TRIETHOHYDRATE. *Triethyl-silicol.*

$$\mathbf{Si}Et_3Ho.$$

Molecular weight =132·5. *Molecular volume* ☐☐. 1 *litre of the vapour weighs* 66·25 *criths. Boils at* 153°·5. *Sp. gr. of liquid* ·8709 *at* 0°.

Preparation. 1. By digesting silicic triethoethylate with water at 200°:—

$$\underset{\substack{\text{Silicic}\\ \text{triethoethylate.}}}{\mathbf{Si}Et_3Eto} + \mathbf{O}H_2 = \underset{\substack{\text{Silicic}\\ \text{triethohydrate.}}}{\mathbf{Si}Et_3Ho} + \underset{\text{Alcohol.}}{\mathbf{O}EtH.}$$

2. By the action of aqueous ammonia upon silicic chlortriethide:—

$$\underset{\substack{\text{Silicic}\\ \text{chlortriethide.}}}{\mathbf{Si}Et_3Cl} + \mathbf{O}H_2 + \mathbf{N}H_3 = \underset{\substack{\text{Silicic}\\ \text{triethohydrate}}}{\mathbf{Si}Et_3Ho} + \mathbf{N}H_4Cl.$$

SILICOPROPIONIC ACID.

$$\left\{\begin{array}{l}\mathbf{C}MeH_2\\ \mathbf{Si}OHo\end{array}\right. .$$

Preparation.—1. This acid, which contains the new negative radical $\mathbf{Si}OHo$ (that is to say, oxatyl in which carbon is replaced by silicon), is prepared from silicic chlortriethylate by the following series of reactions:—

1st. Silicic chlortriethylate is treated with zincic ethide and sodium, and thus converted into silicic ethotriethylate by the following reaction:—

$$\underset{\substack{\text{Silicic}\\\text{chlortriethylate.}}}{2SiClEto_3} + \underset{\substack{\text{Zincic}\\\text{ethide.}}}{ZnEt_2} = ZnCl_2 + \underset{\substack{\text{Silicic}\\\text{ethotriethylate.}}}{2SiEtEto_3}.$$

2nd. Silicic ethotriethylate, which is a colourless liquid, smelling like camphor and boiling at 158°·5, is now heated with concentrated solution of potassic hydrate, when the following change takes place :—

$$\underset{\substack{\text{Silicic}\\\text{ethotriethylate.}}}{SiEtEto_3} + KHo + OH_2 = \underset{\substack{\text{Potassic}\\\text{silicopropionate.}}}{SiEtOKo} + \underset{\text{Alcohol.}}{3EtHo}.$$

3rd. From the potassium salt, silicopropionic is obtained by the addition of hydrochloric acid.

2. By heating silicic ethotriethylate with acetylic chloride to 180°, silicic ethotrichloride is produced :—

$$\underset{\substack{\text{Silicic}\\\text{ethotriethylate.}}}{SiEtEto_3} + \underset{\substack{\text{Acetylic}\\\text{chloride.}}}{3\left\{\begin{matrix}CH_3\\COCl\end{matrix}\right.} = \underset{\substack{\text{Silicic}\\\text{ethotrichloride.}}}{SiEtCl_3} + \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{3\left\{\begin{matrix}CH_3\\COEto\end{matrix}\right.}$$

By the subsequent action of water upon the silicic ethotrichloride, pure silicopropionic acid is obtained as a white insoluble powder resembling silica :—

$$\underset{\substack{\text{Silicic}\\\text{ethotrichloride.}}}{SiEtCl_3} + 2OH_2 = \underset{\substack{\text{Silicopropionic}\\\text{acid}}}{SiEtOHo} + 3HCl.$$

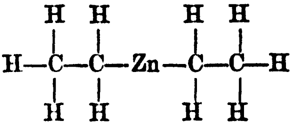
CHAPTER XXXII.

ORGANOMETALLIC BODIES.

This term is applied to a family of compounds in which an organic radical is united directly with a metal; and it serves to distinguish them from other organic compounds containing metals, in which the metal and organic radical are indirectly united or linked to each other.

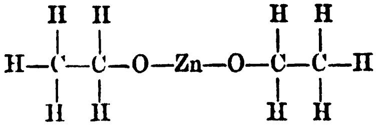
Thus zincic ethide is an organometallic body, while zincic ethylate and zincic succinate are organic bodies containing metals :—

Zincic ethide... $\mathbf{Zn}Et_2$.



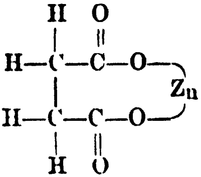
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Zn-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Zincic ethylate... $\mathbf{Zn}Eto_2$.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-Zn-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

Zincic succinate .. $\left\{\begin{matrix}\mathbf{C}O- \\ \mathbf{C}_2H_4 \\ \mathbf{C}O-\end{matrix}\right. Zno''$.



Many organic compounds containing metals are the derivatives of organometallic bodies; thus zincic ethide by oxidation yields zincic ethylate—

$$\underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + O_2 = \underset{\text{Zincic ethylate.}}{\mathbf{Zn}Eto_2};$$

and by further oxidation zincic ethylate can be converted into zincic acetate—

$$\underset{\text{Zincic ethylate.}}{\begin{matrix}\mathbf{C}MeH_2 \\ \mathbf{C}MeH_2\end{matrix}Zno''} + 2O_2 = \underset{\text{Zincic acetate.}}{\begin{matrix}\mathbf{C}MeO \\ \mathbf{C}MeO\end{matrix}Zno''} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

Another instance of the derivation of organic bodies containing metals from organometallic bodies is seen in the formation of potassic propionate by the action of potassic ethide upon carbonic anhydride :—

$$\underset{\text{Potassic ethide.}}{\mathbf{C}MeH_2K} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} = \underset{\text{Potassic propionate.}}{\left\{\begin{matrix}\mathbf{C}MeH_2 \\ \mathbf{C}OKo\end{matrix}\right.}.$$

Formation of organometallic bodies.

Organometallic bodies are produced in a large number of reactions, which, however, may be classed under the following four heads:—

I. By the union of monad positive radicals *in statu nascenti* with a metal, or by the coalescence of a metal with the iodide of a monad positive radical.

Thus, when zinc and ethylic iodide are heated together to 100° in closed vessels, zincic ethide is formed:—

$$\underset{\text{Ethylic iodide.}}{2EtI} + Zn_2 = \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2}.$$

Sometimes light may be employed instead of heat to effect this change, as in the case of the organo-tin compounds. In the formation of organo-mercury compounds by this method, light is indispensable to the reaction:—

$$\underset{\text{Ethylic iodide.}}{EtI} + Hg = \underset{\text{Mercuric ethiodide.}}{\mathbf{Hg}EtI}.$$

II. By the action of the respective metals alloyed with potassium or sodium upon the iodides or, in rare cases, the bromides of the monad positive radicals.

By this process there is less tendency to form compounds containing both positive radicals and negative elements. Potassium or sodium compounds are never produced in this reaction, because they cannot exist in the presence of ethylic iodide or its homologues. This process is well adapted for the formation of arsenic, antimony, tin, mercury, lead, bismuth, and tellurium compounds:—

$$\underset{\text{Ethylic iodide.}}{4EtI} + \underset{\text{Tin sodium alloy.}}{\mathbf{Sn}Na_4} = \underset{\text{Stannic ethide.}}{\mathbf{Sn}Et_4} + \underset{\text{Sodic iodide.}}{4NaI}.$$

$$\underset{\text{Ethylic iodide.}}{2EtI} + \underset{\text{Sodium amalgam.}}{\mathbf{Hg}Na_2} = \underset{\text{Mercuric ethide.}}{\mathbf{Hg}Et_2} + \underset{\text{Sodic iodide.}}{2NaI}.$$

$$\begin{array}{ccccccc} 2C_{10}H_7Br & + & \mathbf{Hg}Na_2 & = & \mathbf{Hg}(C_{10}H_7)_2 & + & 2NaBr. \\ \text{Naphthylic bromide (bromonaphthaline).} & & \text{Sodium amalgam.} & & \text{Mercuric naphthide.} & & \text{Sodic bromide.} \end{array}$$

III. By the action of the zinc compounds of the monad positive radicals upon the haloid compounds, either of the metals themselves, or of their organo- derivatives.

For the production of organometallic bodies containing less positive metals than zinc, this method is generally the most convenient, and is of most universal application. Compounds containing mercury, tin, lead, antimony, and arsenic have been thus produced; but the process has failed when applied to the haloid compounds of copper, silver, platinum, and iron; for, although these bodies are violently acted upon, the organic radicals do not unite with the metal.—

$$\begin{array}{ccccccc} \mathbf{Sn}Cl_4 & + & \mathbf{Zn}Et_2 & = & \mathbf{Sn}Et_2Cl_2 & + & \mathbf{Zn}Cl_2. \\ \text{Stannic chloride.} & & \text{Zincic ethide} & & \text{Stannic dichlorethide} & & \text{Zincic chloride.} \end{array}$$

$$\begin{array}{ccccccc} \mathbf{Sn}Cl_4 & + & 2\mathbf{Zn}Et_2 & = & \mathbf{Sn}Et_4 & + & 2\mathbf{Zn}Cl_2. \\ \text{Stannic chloride} & & \text{Zincic ethide} & & \text{Stannic ethide} & & \text{Zincic chloride.} \end{array}$$

$$\begin{array}{ccccccc} 2\mathbf{Hg}EtI & + & \mathbf{Zn}Et_2 & = & 2\mathbf{Hg}Et_2 & + & \mathbf{Zn}I_2. \\ \text{Mercuric ethiodide.} & & \text{Zincic ethide} & & \text{Mercuric ethide} & & \text{Zincic iodide.} \end{array}$$

IV. By the displacement of a metal in an organometallic compound by another and more positive metal.

This method has been successfully employed for the formation of the organo- compounds of potassium, sodium, lithium, aluminium, and zinc. In the first three cases the reaction takes place at ordinary temperatures, some of the original compound entering into the composition of the resulting organometallic body:—

$$\begin{array}{ccccccc} 3\mathbf{Zn}Et_2 & + & Na_2 & = & 2ZnNaEt_3 & + & Zn. \\ \text{Zincic ethide.} & & & & \text{Sodic zincic ethide.} & & \end{array}$$

$$\begin{array}{ccccccc} 3\mathbf{Hg}Et_2 & + & Al_2 & = & '\mathbf{Al}'''_2Et_6 & + & 3Hg. \\ \text{Mercuric ethide.} & & & & \text{Aluminic ethide.} & & \end{array}$$

$$\begin{array}{ccccccc} \mathbf{Hg}Ay_2 & + & Zn & = & \mathbf{Zn}Ay_2 & + & Hg. \\ \text{Mercuric amylide.} & & & & \text{Zincic amylide.} & & \end{array}$$

Reactions of organometallic bodies.

1. The most interesting reaction of the *organo- compounds of the monad metals* is their transformation into salts of normal fatty acids by the action of carbonic anhydride (see p. 118).

2. The *organo- compounds of potassium and sodium* decompose the iodides of the monad positive radicals in the cold, forming hydrides and dyad radicals :—

$$\underset{\text{Sodic ethide.}}{\mathbf{C}_2H_5Na} + \underset{\text{Ethylic iodide}}{\mathbf{C}_2H_5I} = \underset{\text{Sodic iodide}}{NaI} + \underset{\text{Ethylic hydride.}}{\mathbf{C}_2H_5H} + \underset{\text{Ethylene.}}{\mathbf{C}_2H_4.}$$

3. The *organo- compounds of zinc* are decomposed by water, with formation of the hydrides of the radicals :—

$$\underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + \underset{\text{Water}}{2\mathbf{O}H_2} = \underset{\text{Zincic hydrate}}{\mathbf{Zn}Ho_2} + \underset{\text{Ethylic hydride}}{2EtH.}$$

4. By the slow action of dry oxygen, they pass through two stages of oxidation :—

$$\underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + O = \underset{\text{Zincic etho-ethylate.}}{\mathbf{Zn}EtEto;}$$

$$\underset{\text{Zincic etho-ethylate}}{\mathbf{Zn}EtEto} + O = \underset{\text{Zincic ethylate}}{\mathbf{Zn}Eto_2.}$$

5. Monad negative elements, such as iodine, remove successively the two atoms of ethyl :—

$$\underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} + I_2 = \underset{\text{Zincic ethiodide}}{\mathbf{Zn}EtI} + \underset{\text{Ethylic iodide}}{EtI:}$$

$$\underset{\text{Zincic ethiodide.}}{\mathbf{Zn}EtI} + I_2 = \underset{\text{Zincic iodide.}}{\mathbf{Zn}I_2} + \underset{\text{Ethylic iodide.}}{EtI.}$$

6. The organo-zinc compounds are extremely useful for the displacement of chlorine or its analogues by ethyl or its homologues :—

$$\underset{\text{Phosphorous trichloride.}}{2\mathbf{P}Cl_3} + \underset{\text{Zincic ethide.}}{3\mathbf{Zn}Et_2} = \underset{\text{Triethylphosphine.}}{2\mathbf{P}Et_3} + \underset{\text{Zincic chloride.}}{3\mathbf{Zn}Cl_2.}$$

$$\underset{\text{Silicic chloride.}}{\mathbf{Si}Cl_4} + \underset{\text{Zincic ethide.}}{2\mathbf{Zn}Et_2} = \underset{\text{Silicic ethide.}}{\mathbf{Si}Et_4} + \underset{\text{Zincic chloride.}}{2\mathbf{Zn}Cl_2}.$$

$$\underset{\text{Chlorether}}{2\left\{\begin{array}{l}\mathbf{C}_2H_4Cl\\ O\\ \mathbf{C}_2H_4Cl\end{array}\right.} + \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} = \underset{\text{Ethylo-chlorether.}}{2\left\{\begin{array}{l}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Cl\end{array}\right.} + \underset{\text{Zincic chloride.}}{\mathbf{Zn}Cl_2}:$$

$$\underset{\text{Ethylo-chlorether.}}{2\left\{\begin{array}{l}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Cl\end{array}\right.} + \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} = \underset{\text{Diethylated ethylic ether.}}{2\left\{\begin{array}{l}\mathbf{C}_2H_4Et\\ O\\ \mathbf{C}_2H_4Et\end{array}\right.} + \underset{\text{Zincic chloride.}}{\mathbf{Zn}Cl_2}.$$

Diethylated ethylic ether is isomeric with butylic ether, and contains the radical methylo-ethylated methyl (see p. 8). By oxidation it would doubtless give methylated acetone (p. 187).

7. Oxygen may also be displaced in a similar manner. Thus:—

$$\underset{\text{Nitric oxide}}{2\mathbf{N}''_2O_2} + \underset{\text{Zincic ethide.}}{\mathbf{Zn}Et_2} = \underset{\text{Zincic dinitro-ethylate}}{\left.\begin{array}{l}\mathbf{N}_2OEt\text{-}O\\ \mathbf{N}_2OEt\text{-}O\end{array}\right]Zn'' \text{ or } \begin{array}{l}\mathbf{N}_2EtO\\ \mathbf{N}_2EtO\end{array}Zno''}.$$

This compound is analogous to zincic propionate, the latter containing two atoms of tetrad carbon in the place of the two tetrad pairs of nitrogen atoms:—

$$\text{Zincic propionate} \ldots \left.\begin{array}{l}\mathbf{C}OEt\text{-}O\\ \mathbf{C}OEt\text{-}O\end{array}\right]Zn'' \text{ or } \begin{array}{l}\mathbf{C}EtO\\ \mathbf{C}EtO\end{array}Zno''.$$

8. An analogous reaction is observed with sulphurous anhydride:—

$$\underset{\text{Sulphurous anhydride.}}{2\mathbf{S}O_2} + \underset{\text{Zincic methide.}}{\mathbf{Zn}Me_2} = \underset{\text{Zincic methyldithionate.}}{\left.\begin{array}{l}\mathbf{S}OMe\text{-}O\\ \mathbf{S}OMe\text{-}O\end{array}\right]Zn'' \text{ or } \begin{array}{l}\mathbf{S}MeO\\ \mathbf{S}MeO\end{array}Zno''}.$$

9. When ethylic borate is acted upon by zincic methide, the ethoxyl becomes replaced by methyl :—

$$\mathbf{B}\text{Eto}_3 + 3\mathbf{Zn}\text{Me}_2 = \mathbf{B}\text{Me}_3 + 3\mathbf{Zn}\text{MeEto}.$$

$\mathbf{B}\text{Eto}_3$	$3\mathbf{Zn}\text{Me}_2$	$\mathbf{B}\text{Me}_3$	$3\mathbf{Zn}\text{MeEto}$
Ethylic borate	Zincic methide.	Boric methide.	Zincic methide ethylate.

10. When ethylic oxalate is heated with zincic ethide, and water afterwards added, ethylic diethoxalate is formed :—

$$\left\{\begin{matrix}\mathbf{C}\text{OEto}\\ \mathbf{C}\text{OEto}\end{matrix}\right. + \mathbf{Zn}\text{Et}_2 + 2\mathbf{O}\text{H}_2 = \left\{\begin{matrix}\mathbf{C}\text{Et}_2\text{Ho}\\ \mathbf{C}\text{OEto}\end{matrix}\right. + \mathbf{Zn}\text{Ho}_2 + \text{EtHo}.$$

$\left\{\begin{matrix}\mathbf{C}\text{OEto}\\ \mathbf{C}\text{OEto}\end{matrix}\right.$	$\mathbf{Zn}\text{Et}_2$	$2\mathbf{O}\text{H}_2$	$\left\{\begin{matrix}\mathbf{C}\text{Et}_2\text{Ho}\\ \mathbf{C}\text{OEto}\end{matrix}\right.$	$\mathbf{Zn}\text{Ho}_2$	EtHo
Ethylic oxalate.	Zincic ethide.	Water.	Ethylic diethoxalate.	Zincic hydrate.	Alcohol.

11. By the action of ammonia, or of certain amines and amides, zincic ethide exchanges its zinc for hydrogen :—

$$\mathbf{Zn}\text{Et}_2 + 2\mathbf{N}\text{H}_3 = \mathbf{Zn}\text{Ad}_2 + 2\text{EtH}.$$

$\mathbf{Zn}\text{Et}_2$	$2\mathbf{N}\text{H}_3$	$\mathbf{Zn}\text{Ad}_2$	2EtH
Zincic ethide.	Ammonia.	Zincic amide.	Ethylic hydride.

12. The organo-zinc compounds, by losing one semimolecule of their organic radical, become monad radicals, as shown by the following formulæ :—

Methylozincic dinitromethylate	$'\mathbf{N}''_2\text{OMe-O-(ZnMe)}$.
Ethylozincic dinitroethylate	$'\mathbf{N}''_2\text{OEt-O-(ZnEt)}$.
Ethylic ethylo-zincic diethoxalate	$\left\{\begin{matrix}\mathbf{C}\text{Et}_2\text{-O-(ZnEt)}\\ \mathbf{C}\text{OEto}\end{matrix}\right.$.

13. *Mercuric ethide*, when treated with bromine, loses one-half of its ethyl, which is displaced by the negative element :—

$$\mathbf{Hg}\text{Et}_2 + \text{Br}_2 = \mathbf{Hg}\text{EtBr} + \text{EtBr}.$$

$\mathbf{Hg}\text{Et}_2$	Br_2	$\mathbf{Hg}\text{EtBr}$	EtBr
Mercuric ethide.		Mercuric ethobromide.	Ethylic bromide.

14. *Mercuric methide*, when submitted to the action of mercuric iodide, yields mercuric methiodide :—

$$\mathbf{Hg}\text{Me}_2 + \mathbf{Hg}\text{I}_2 = 2\mathbf{Hg}\text{MeI}.$$

$\mathbf{Hg}\text{Me}_2$	$\mathbf{Hg}\text{I}_2$	$2\mathbf{Hg}\text{MeI}$
Mercuric methide.	Mercuric iodide.	Mercuric methiodide.

The hydrates corresponding to the mercuric ethobromide and methiodide have been produced. They are powerful caustic bases, of the formulæ

$$\underset{\substack{\text{Mercuric}\\\text{ethohydrate.}}}{\mathbf{Hg}EtHo} \text{ and } \underset{\substack{\text{Mercuric}\\\text{methohydrate.}}}{\mathbf{Hg}MeHo}.$$

15. The *organo-stannous* compounds unite directly with negative elements, passing into stannic bodies :—

$$\underset{\substack{\text{Stannous}\\\text{ethide.}}}{\mathbf{Sn}Et_2} + I_2 = \underset{\substack{\text{Stannic}\\\text{iododiethide.}}}{\mathbf{Sn}Et_2I_2}.$$

16. *Hypostannic organo- compounds* undergo a similar transformation :—

$$\underset{\substack{\text{Hypostannic}\\\text{ethide.}}}{'\mathbf{Sn}'''_2Et_6} + I_2 = \underset{\substack{\text{Stannic}\\\text{iodotriethide.}}}{2\mathbf{Sn}Et_3I}:$$

$$\underset{\substack{\text{Stannic}\\\text{iodotriethide.}}}{\mathbf{Sn}Et_3I} + I_2 = \underset{\substack{\text{Stannic}\\\text{iododiethide.}}}{\mathbf{Sn}Et_2I_2} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{EtI}.$$

17. *Hypostannic ethodiniodide* is formed by the action of iodine upon stannic ethodimethide :—

$$\underset{\substack{\text{Stannic}\\\text{ethodimethide.}}}{2\mathbf{Sn}Et_2Me_2} + I_6 = \underset{\substack{\text{Hypostannic}\\\text{ethodiniodide.}}}{'\mathbf{Sn}'''_2Et_4I_2} + \underset{\substack{\text{Methylic}\\\text{iodide.}}}{4MeI}.$$

18. *Stannic ethide*, when treated with hydrochloric acid, yields stannic chlorotriethide and ethylic hydride :—

$$\underset{\substack{\text{Stannic}\\\text{ethide.}}}{\mathbf{Sn}Et_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} = \underset{\substack{\text{Stannic}\\\text{chlorotriethide.}}}{\mathbf{Sn}Et_3Cl} + \underset{\substack{\text{Ethylic}\\\text{hydride.}}}{EtH}.$$

The oxide and hydrate corresponding to the stannic chlorotriethide are known ; their formulæ are :—

$$\text{Oxide} \ldots \left\{\begin{matrix}\mathbf{Sn}Et_3\\ O\\ \mathbf{Sn}Et_3\end{matrix}\right. ; \text{ Hydrate} \ldots \mathbf{Sn}Et_3Ho.$$

These compounds, and the salts which they form, correspond in composition, constitution, and, to a certain extent, in properties, with the compounds of methyl:—

	Alcohol.	Haloid ether.	Ether.
Methylic	CH_3Ho.	CH_3Cl.	$\left\{\begin{matrix}CH_3\\O\\CH_3\end{matrix}\right.$;
Stanntriethylic......	$SnEt_3Ho$.	$SnEt_3Cl$.	$\left\{\begin{matrix}SnEt_3\\O\\SnEt_3\end{matrix}\right.$.

19. *Stannic chlorodiethide* is readily reduced to stannous ethide by the action of zinc:—

$$\underset{\text{Stannic chlorodiethide.}}{SnEt_2Cl_2} + Zn = \underset{\text{Stannous ethide.}}{SnEt_2} + \underset{\text{Zincic chloride.}}{ZnCl_2}.$$

20. *Perplumbic ethide* resembles stannic ethide in its reactions; thus with hydrochloric acid it yields perplumbic chlorotriethide and ethylic hydride:—

$$\underset{\text{Perplumbic ethide.}}{PbEt_4} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Perplumbic chlorotriethide.}}{PbEt_3Cl} + \underset{\text{Ethylic hydride.}}{EtH}.$$

21. *Perplumbic triethohydrate* ($PbEt_3Ho$) is a powerful base, forming salts with acids.

22. The *organo-tellurium compounds* form oxides and salts. The following are the formulæ of tellurium ethide and some of its compounds:—

Tellurium ethide	$TeEt_2$.
Tellurous diethoxide..................	$TeEt_2O$.
Tellurous diethiodide	$TeEt_2I_2$.
Tellurous diethosulphate............	$TeEt_2(S^{vi}O_4)''$.

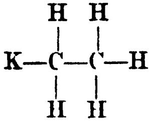
Constitution of Organometallic Bodies.

The organometallic compounds are constituted on the types of the metals they contain. It was, in fact, the study of these bodies which first led to the doctrine of the atomicity of elements. They afford striking examples of monad, dyad, triad, tetrad, pentad, and hexad types.

The organic derivatives of the monad metals are formed on the type of potassic chloride (KCl) :—

K—Cl

Potassic chloride.



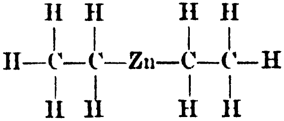
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ K & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Potassic ethide.

The organo-zinc, cadmium, magnesium, and mercury compounds are formed upon the type of zincic chloride $(\mathbf{Zn}Cl_2)$:—

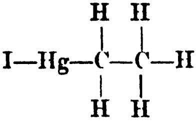
Cl—Zn—Cl

Zincic chloride.



$$\begin{array}{ccccccccccccc} & & H & & H & & & & H & & H & & \\ & & | & & | & & & & | & & | & & \\ H & - & C & - & C & - & Zn & - & C & - & C & - & H \\ & & | & & | & & & & | & & | & & \\ & & H & & H & & & & H & & H & & \end{array}$$

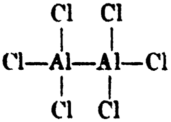
Zincic ethide.



$$\begin{array}{ccccccccc} & & & & H & & H & & \\ & & & & | & & | & & \\ I & - & Hg & - & C & - & C & - & H \\ & & & & | & & | & & \\ & & & & H & & H & & \end{array}$$

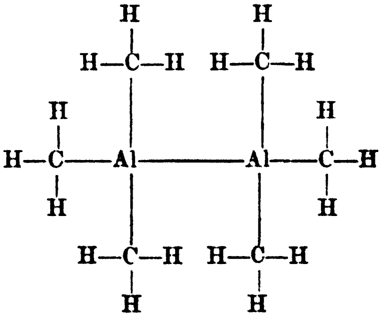
Mercuric iodethide.

The organo-aluminic compounds are formed upon the type of aluminic chloride $('\mathbf{Al}'''_2Cl_6)$:—



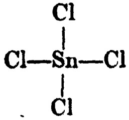
$$\begin{array}{ccccccc} & & Cl & & Cl & & \\ & & | & & | & & \\ Cl & - & Al & - & Al & - & Cl \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$

Aluminic chloride.



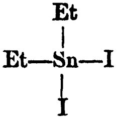
Aluminic methide.

The organo-tin compounds are formed upon the three types $''\mathbf{Sn}''Cl_2$, $'\mathbf{Sn}'''_2Cl_6$, and $\mathbf{Sn}Cl_4$,—the first resembling the zincic chloride type, and the second the aluminic chloride type (see p. 232) :—



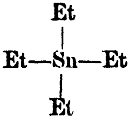
$$\begin{array}{c} \text{Cl} \\ | \\ \text{Cl—Sn—Cl} \\ | \\ \text{Cl} \end{array}$$

Stannic chloride.



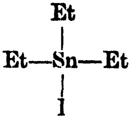
$$\begin{array}{c} \text{Et} \\ | \\ \text{Et—Sn—I} \\ | \\ \text{I} \end{array}$$

Stannic iododiethide.



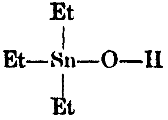
$$\begin{array}{c} \text{Et} \\ | \\ \text{Et—Sn—Et} \\ | \\ \text{Et} \end{array}$$

Stannic ethide.



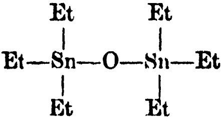
$$\begin{array}{c} \text{Et} \\ | \\ \text{Et—Sn—Et} \\ | \\ \text{I} \end{array}$$

Stannic iodotriethide.



$$\begin{array}{l} \quad\;\;\text{Et} \\ \quad\;\;\; | \\ \text{Et—Sn—O—H} \\ \quad\;\;\; | \\ \quad\;\;\text{Et} \end{array}$$

Stannic triethohydrate.



$$\begin{array}{ccccc} & \text{Et} & & \text{Et} & \\ & | & & | & \\ \text{Et—} & \text{Sn} & \text{—O—} & \text{Sn} & \text{—Et} \\ & | & & | & \\ & \text{Et} & & \text{Et} & \end{array}$$

Distannic hexethoxide.

The inorganic types of the organo-tellurium series are $\mathbf{Te}\text{Cl}_2$ and $\mathbf{Te}\text{O}_2$:—

Cl—Te—Cl

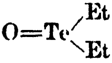
Tellurium chloride.

O=Te=O

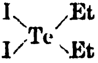
Tellurous oxide.

Et—Te—Et

Tellurium ethide.

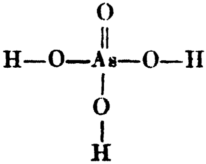


Tellurous diethoxide.



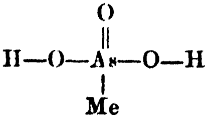
Tellurous diethiodide.

The organo-arsenic, antimony, and bismuth compounds are derived from the types '$\mathbf{As}''_2\text{S}''_2$, $\mathbf{As}\text{Cl}_3$, $\mathbf{As}\text{OHo}_3$, $\mathbf{Sb}\text{Cl}_3$, $\mathbf{Sb}\text{Cl}_5$, $\mathbf{Bi}\text{Cl}_3$, and $\mathbf{Bi}\text{O}_2\text{Ho}$ (see pp. 204, 211, and 214) :—



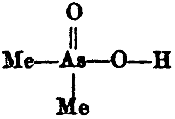
$$\begin{array}{c} \text{O} \\ \| \\ \text{H—O—As—O—H} \\ | \\ \text{O} \\ | \\ \text{H} \end{array}$$

Arsenic acid.



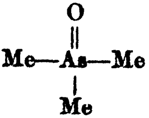
$$\begin{array}{c} \text{O} \\ \| \\ \text{H—O—As—O—H} \\ | \\ \text{Me} \end{array}$$

Monomethylarsenic acid.



$$\begin{array}{l} \quad\;\;\;\text{O} \\ \quad\;\;\;\; \| \\ \text{Me—As—O—H} \\ \quad\;\;\;\; | \\ \quad\;\;\;\text{Me} \end{array}$$

Cacodylic acid.



$$\begin{array}{c} \text{O} \\ \| \\ \text{Me—As—Me} \\ | \\ \text{Me} \end{array}$$

Arsenic oxytrimethide.

The effect of the substitution of positive for negative radicals in compounds is strikingly exhibited in the case of arsenic acid, $\mathbf{As}OHo_3$, as illustrated in the above graphic representations. By the substitution of one semimolecule of methyl for hydroxyl, a well-defined acid (less negative, however, than arsenic acid) is produced, monomethylarsenic acid, $\mathbf{As}OMeHo_2$. By the replacement of a second semimolecule of hydroxyl by methyl, a very feeble acid, cacodylic acid, $\mathbf{As}OMe_2Ho$, is obtained. By the replacement of the third semimolecule of hydroxyl by methyl, the acid properties are completely destroyed, a feeble base, the arsenic oxytrimethide, being formed, $\mathbf{As}OMe_3$. Finally, by the substitution of methyl and hydroxyl for the remaining atom of oxygen there is produced a powerful base, tetramethylarsenic hydrate, $\mathbf{As}Me_4Ho$.

The following is a list of the principal organometallic bodies at present known:—

I. Organo- compounds containing monad metals:—

Potassio-zincic methide	$KMe,\mathbf{Zn}Me_2$.
Potassio-zincic ethide	$KEt,\mathbf{Zn}Et_2$.
Sodio-zincic ethide.................	$NaEt,\mathbf{Zn}Et_2$.
Lithio-zincic ethide	$LiEt,\mathbf{Zn}Et_2$.
Lithio-mercuric ethide	$LiEt,\mathbf{Hg}Et_2$.

II. Organo- compounds containing dyad metals:—

Magnesic ethide....................	$\mathbf{Mg}Et_2$.
Zincic methide	$\mathbf{Zn}Me_2$.
Zincic ethide	$\mathbf{Zn}Et_2$.
Zincic amylide	$\mathbf{Zn}Ay_2$.
Mercuric methide	$\mathbf{Hg}Me_2$.
Mercuric ethide	$\mathbf{Hg}Et_2$.
Mercuric methiodide	$\mathbf{Hg}MeI$.
Mercuric ethonitrate..............	$\mathbf{Hg}Et(N^{v}O_3)$.
Stannous ethide	$''\mathbf{Sn}''Et_2$.
Tellurium methide	$\mathbf{Te}Me_2$.

III. Organo- compounds containing triad metals:—

These compounds belong to the 11th family of organic bodies, and have been treated of at p. 202.

IV. Organo- compounds of tetrad metals:—

Stannic methide	$\mathbf{Sn}Me_4$.
Stannic iodotrimethide	$\mathbf{Sn}Me_3I$.
Stannic iododimethide	$\mathbf{Sn}Me_2I_2$.
Hypostannic ethide	$'\mathbf{Sn}'''_2Et_6$.
Stannic ethylodimethide	$\mathbf{Sn}Et_2Me_2$.
Stannic phenyl-triethide	$\mathbf{Sn}PhEt_3$.
Stannic ethophenyl-dichloride	$\mathbf{Sn}PhEtCl_2$.
Hypostannic ethodiiodide	$'\mathbf{Sn}'''_2Et_4I_2$.
Perplumbic ethide	$\mathbf{Pb}Et_4$.
Perplumbic chlorotriethide	$\mathbf{Pb}Et_3Cl$.

V. Organo- compounds of pentad metals:—

These bodies belong to the 11th family of organic compounds, and have been already treated of at pp. 211 and 214.

INDEX TO VOL. II.

Acetamide, 206.
Acetic series of acids, 114.
  „ series of acids, relations of, to acrylic series, 132.
  „ series of acids, relations of, to lactic series, 142.
Acetic series, relations of succinic series to, 162.
Acetone, 187.
  „ diethylated, 187.
  „ dimethylated, 187.
  „ ethylated, 186
  „ methylated, 187.
Acetyl, 25.
Acetylene, 21.
  „ series of radicals, 21.
Acetylic chloride, 125.
  „ nitride, 210.
Acetylide of copper, 23.
Acid, acetic, 123.
  „ aceto-lactic, 135, 137.
  „ acetonic, 150.
  „ aconitic, 178.
  „ acrylic, 81, 111, 133.
  „ adipic, 160.
  „ alizaric, 177.
  „ alpha-cymic, 155.
  „ alpha-toluylic, 155.
  „ alpha-xylic, 155.
  „ amidocaproic, 150.
  „ amidodinitrophenylic, 69
  „ anchoic, 160.
  „ angelic, 130.
  „ anisic, 156.
  „ anthraflavic, 177.
  „ anthraquinonic, 176.
  „ aposorbic, 84.
  „ arachidic, 116.
  „ atropic, 156.
  „ behenic, 116.
  „ benzenic, 155.
  „ benzoic, 155, 157, 180.
  „ brassic, 130.
  „ bromotricarballylic, 178.
Acid, bromphenylic, 69.
  „ butyric, 126.
  „ cacodylic, 205, 214, 233, 234.
  „ capric, 116.
  „ caproic, 115.
  „ caprylic, 115.
  „ carbolic, 67.
  „ carbomethylic, 144.
  „ cerotic, 116.
  „ chloropropionic, 147.
  „ cimicic, 130.
  „ cinnamic, 155.
  „ citraconic, 166
  „ citric, 178.
  „ collinic, 155.
  „ convolvulinoleic, 151.
  „ cresotic, 156.
  „ crotonic, 130.
  „ β crotonic, 131.
  „ cuminic, 155.
  „ cyanic, 32.
  „ cyanuric, 32.
  „ damaluric, 130.
  „ damolic, 130.
  „ desoxalic, 179.
  „ dextrotartaric, 173.
  „ diamylacetic, 129.
  „ dibromosuccinic, 168.
  „ dichloracetic, 124.
  „ dichlorphenylic, 69.
  „ diethacetic, 129.
  „ diethoxalic, 138.
  „ dimethacetic, 128.
  „ dimethoxalic, 138, 150.
  „ dinitrophenylic, 69.
  „ disulphanthraquinonic, 176.
  „ doeglic, 130.
  „ elaidic, 130.
  „ erucic, 130.
  „ erythric, 76.
  „ ethacetic, 126.
  „ ethomethoxalic, 138.
  „ ethylcrotonic, 131.
  „ ethylglycollic, 150.

Acid, ethyl-lactic, 137.
„ formic, 121.
„ fulminuric, 32.
„ fumaric, 166.
„ gaidic, 130.
„ gallic, 157.
„ glyceric, 80, 152.
„ glycollamic, 157.
„ glycollic, 71, 91, 136.
„ glycomalic, 173.
„ glyoxalic, 151.
„ glyoxylic, 152.
„ hemimellitic, 180.
„ hexahydrophthalic, 175.
„ hippuric, 157.
„ homolactic, 145.
„ homotartaric, 173.
„ hyænasic, 116.
„ hydrocyanic, 27, 49.
„ hydroferrocyanic, 31.
„ hypogæic, 130.
„ isobutyric, 128.
„ isochloropropionic, 149.
„ isodibromosuccinic, 168.
„ isomaleic, 166.
„ isophthalic, 180.
„ isopropacetic, 115, 127.
„ isosuccinic, 166.
„ itaconic, 166.
„ itatartaric, 171.
„ jalapinoleic, 151.
„ lactamic, 109, 147.
„ lactic, 109, 143, 147, 148.
„ lævotartaric, 174.
„ lauric, 116.
„ lecanoric, 76.
„ leucic, 136.
„ maleic, 166.
„ malic, 164, 172.
„ malonic, 148, 160.
„ mannitic, 84.
„ margaric, 116.
„ melissic, 116.
„ mellitic, 179.
„ mellophanic, 180.
„ mesaconic, 166.
„ metagallic, 83.
„ metatartaric, 174.
„ methacetic, 125.
„ methacrylic, 131.
„ methethacetic, 127.
„ methylcrotonic, 131.
„ methylglycollic, 137, 145.
„ methyl-lactic, 135.
Acid, monochloracetic, 124.
„ monomethylarsenic, 214, 233, 234.
„ moringic, 130.
„ mucic, 84.
„ myristic, 116.
„ nitrophenylic, 69.
„ œnanthylic, 115.
„ oleic, 134.
„ orsellinic, 76.
„ oxalic, 34.
„ oxamic, 35.
„ oxybutyric, 136.
„ oxymethyl-phenylformic, 156.
„ palmitic, 116.
„ paralactic, 139, 145.
„ paraleucic, 139.
„ paraphloretic, 156.
„ pelargonic, 115
„ perchlorphenylic, 69.
„ phenoic, 155.
„ phenomalic, 81.
„ phenylic, 68.
„ phthalic, 180.
„ physetoleic, 130.
„ picramic, 69.
„ picric, 69.
„ pimelic, 160.
„ prehnitic, 180.
„ propionic, 125.
„ propylacetic, 127.
„ pyrotauric, 171.
„ pyromellitic, 179, 180.
„ pyrotartaric, 160, 171.
„ pyroterebic, 130.
„ pyruvic, 151.
„ racemic, 174.
„ ricinoleic, 151.
„ roccellic, 160.
„ saccharic, 84.
„ salicylic, 156.
„ sebacic, 160.
„ silicopropionic, 220.
„ stearic, 116.
„ suberic, 160.
„ succinethylic, 189.
„ succinic, 163.
„ sulphamylic, 88.
„ sulphomethylic, 87, 99.
„ sulphovinic, 88.
„ tannic, 158.
„ tartaric, 83, 173.
„ tartaric (inactive), 174.
„ tartronic, 80, 172.

Acid, tartrophthalic, 176.
„ terephthalic, 180.
„ tetrahydrophthalic, 176.
„ thymotic, 156.
„ toluylic, 155.
„ tricarballylic, 177, 178.
„ trichloracetic, 124.
„ trichlorphenylic, 69.
„ trimellitic, 180.
„ trimesic, 180.
„ trimethacetic, 129.
„ trinitro-orcinic, 76.
„ trinitrophenylic, 69.
„ valerianic, 126.
„ valeric, 126.
„ valeric (isomeric forms), 126.
„ valerolactic, 136.
„ xylic, 155.
Acids, acetic or fatty series of, 114.
„ acetoid series of, 159.
„ acrylic series of, 130.
„ benzoic or aromatic series of, 153.
„ classification of, 113.
„ derivation of, from alcohols, 113.
„ dibasic, 158.
„ dibasic, formation of, 158.
„ dibasic, reactions of, 158.
„ dibasic, fumaric or acryloid series of, 166.
„ dibasic, other series of, 175.
„ dibasic, succinic or acetoid series of, 159.
„ dibasic, tartaric or glyoxyloid series of, 173.
„ fumaric or acryloid series of, 166.
„ glyoxylic series of, 152.
„ hexabasic, 179.
„ lactic series of, 134.
„ lactic series of, classification of, 135.
„ lactic series of, definition of, 134.
„ lactic series of, relations to acetic series, 142.
„ lactic series of, relations to acrylic series, 142.
„ law of basicity of, 113.
„ malic or lactoid series of, 172.
„ monobasic, 113.
„ normal fatty, ascent of the series, 121.
Acids, normal fatty, formation of, 117.
„ normal fatty, relations of, to $C_nH_{2n+1}Ho$ alcohols, 120.
„ normal fatty, relations of, to C_nH_{2n+1} radicals, 119.
„ normal fatty, relations of, to each other, 121.
„ normal, of acetic series, 115.
„ normal, of acrylic series, 130.
„ normal, of acrylic series, formation of, 131.
„ normal of fatty series, formation of, 117.
„ normal, of fatty series, occurrence of, 116.
„ normal, of lactic series, formation of, 141.
„ of acrylic series, relations of, to acetic series, 132.
„ of lactic series, isomerism of, 143.
„ olefine, of acrylic series, 131.
„ olefine, of acrylic series, formation of, 132.
„ olefine, of lactic series, formation of, 141.
„ oleic series of, 130.
„ organic, 112.
„ pyruvic series of, 151.
„ secondary fatty, 128.
„ secondary, of acrylic series, 131.
„ secondary, of acrylic series, formation of, 131.
„ secondary of lactic series, 137.
„ secondary, of lactic series, formation of, 141.
„ succinic series of, 159.
„ succinic series of, relations to acetic series, 162.
„ succinic series of, relations to dyad radicals, 161.
„ succinic series of, relations to lactic series and to glycols, 161.
„ tertiary fatty, 129.
„ tetrabasic, 179.
„ tribasic, 177.
„ tribasic, aconitic or acryloid series, 177.
„ tribasic, citric or lactoid series, 178.

Acids, tribasic, tricarballylic or acetoid series, 177.
Acridine, 200.
Acrolein, 80, 110.
Acryl, 25.
Acrylic series of acids, 130.
Acrylic series of acids, relations of, to lactic series, 142.
Acryloid or fumaric series of acids, 166.
,, series of acids, isomerism in, 166.
Alanin, 109, 147.
Alcohol, allylic, 65.
,, amylic, 52, 60.
,, benzylic, 67.
,, butylic, 52, 59.
,, caproylic, 52.
,, caprylic, 53.
,, cerotic, 53.
,, cetylic, 53.
,, cresylic, 67, 70.
,, cumylic, 67.
,, decatylic, 53.
,, dimethylphenylic, 67.
,, ethylenic, 71.
,, ethylic, 52, 57.
,, heptylic, 53.
,, hexylic, 52.
,, isamylic, 52.
,, isobutylic, 52.
,, isopropylic, 60.
,, melissic, 53.
,, methylic, 52, 56.
,, nonylic, 53.
,, octylic, 53.
,, œnanthylic, 53.
,, pentahydric, 84.
,, pentylic, 52.
,, phenylic, tertiary, 67, 68.
,, phenylic, substitution products of, 69.
,, propylic, 52, 59, 62.
,, pseudamylic, 52.
,, pseudobutylic, 62.
,, pseudohexylic, 60.
,, stanntriethylic, 231.
,, sulphur, 59.
,, sycocerylic, 67.
,, tetrahydric, 83.
,, tetrylic, 52.
,, thymylic, 67.
,, vinylic, 64.
,, xylylic, 67.
Alcoholates, 58.
Alcohols, 49.
,, dihydric, 51.
,, dihydric, glycol series, 70.
,, dihydric, orcin series, 74.
,, monohydric, 50, 52.
,, monohydric, methyl series, 52.
,, monohydric, methyl series, normal, 52.
,, monohydric, methyl series, secondary, 52, 60.
,, monohydric, methyl series, tertiary, 52, 62.
,, monohydric, phenyl series, 66.
,, monohydric, phenyl series, normal, 66, 67.
,, monohydric, phenyl series, tertiary, 67.
,, monohydric, vinyl series, 63.
,, polyhydric, 83.
,, relations of, 53.
,, relations of, to fatty acids, 120.
,, secondary, oxidation of, 62.
,, trihydric, 51.
,, trihydric, glycerin series, 77.
,, trihydric, pyrogallic series, 81.
Aldehyde, acetic, 108.
,, acrylic, 110.
,, benzoic, 111.
,, butyric, 108.
,, capric, 108.
,, cuminic, 111.
,, euodic, 108.
,, formic, 108.
,, lauric, 108.
,, œnanthic, 108.
,, palmitic, 108.
,, propionic, 108.
,, salicylic, 156.
,, valeric, 108.
Aldehydes, 105.
,, definition of, 105.
,, derived from the $C_nH_{2n+1}Ho$ alcohols, 108.
,, from the $C_nH_{2n-1}Ho$ alcohols, 110.

Aldehydes from the C_nH_{2n-7}Ho alcohols, 111.
  „ preparation of, 105.
  „ reactions of, 107.
Alizarin, 176.
Alkalamides, 209.
  „ constitution of, 209.
Alkaloids, artificial, 191.
  „ from cinchona, 201.
  „ from nightshade, 202.
  „ from nux vomica, 202.
  „ from opium, 201.
  „ from tea, coffee, and cocoa, 202.
  „ from tobacco, 202.
  „ the natural, 201.
Allyl, 13.
Allylamine, 192.
Allylene, 21.
Allylic iodide, 79, 94.
  „ sulphide, 66.
  „ sulphocyanate, 66.
Aluminic ethide, 226.
Amarine, 200.
Amides, 190, 205.
  „ definition of, 205.
Amines, 191.
  „ classification of, 191.
  „ diacid salts of, 213.
  „ monacid salts of, 213.
  „ normal salts of, 212.
  „ salts of, 212.
Ammonia-boric ethide, 218.
  „ methide, 216.
Ammonia type, 4, 5.
Ammonic chloride type, 4, 5.
Amoxyl, 5.
Amygdalin, 112.
Amyl, 11.
Amylamine, 192.
Amyl benzol, 14.
Amylene, 17.
Amylenic chloride, 103.
  „ bromide, 103.
  „ oxide, 90.
Amyl glycerin, 78.
Amylic iodide, 102.
Amylide, zincic, 234.
Amyl toluol, 14.
  „ xylol, 15.
Anhydride, acetic, 182.
  „ acetobenzoic, 183.
  „ benzoic, 183.
Anhydride, butyric, 182.
  „ caproic, 183.
  „ caprylic, 183.
  „ lactic, 183.
  „ œnanthylic, 183.
  „ palmitic, 183.
  „ pelargonic, 183.
  „ propionic, 182.
  „ silico-formic, 218.
  „ succinic, 184.
  „ valeric, 182.
Anhydrides, 181.
  „ conversion into acids, 182, 183.
  „ definition of, 181.
  „ of the dihydric dibasic acids, 184.
  „ of the dihydric monobasic acids, 183.
  „ of the monohydric monobasic acids, 182.
Aniline, 191.
Aniline blue, 198.
  „ violet, 198.
Anthracene, 176.
Anthraquinone, 176.
Antimonic acids, organic, 215.
Antimony, organic compounds of, 190.
Arbutin, 75.
Aricine, 201.
Aromatic series of acids, 153.
Arsenic acids, organic, 214.
Arsenic, organic compounds of, 190.
Arsenic oxydichlormethide, 214.
  „ oxytrimethide, 233, 234.
  „ tetrachlormethide, 214.
  „ trimetho-dichloride, 214.
  „ trimethoxide, 214.
Arsenious oxybases, 204.
Arsine triethyl, 204.
  „ trimethyl, 204.
Arsines, 190, 202.
  „ salts of, 214.
Ascent of the alcohol series, 55.
Atropine, 202.
Azobenzol, 48.

Bases, caustic antimony, 211.
  „ caustic arsenic, 211.
  „ caustic nitrogen, 211.
  „ caustic phosphorus, 211.
  „ imidogen, 193.

Bases, organic, 191.
 „ oxyantimonic, 212.
 „ oxyarsenic, 211.
Benzamide, 206.
Benzene, 44.
Benzine, 44.
Benzoic series of acids, 153.
Benzol, 42, 44.
 „ bromocompounds of, 45.
 „ chlorocompounds of, 47.
 „ substitution derivatives of, 43.
Benzonitrile, 154.
Benzophenone, 188.
Benzoyl, hydride of, 111.
Benzyl, 14.
Betaorcin, 74.
Bicarburet of hydrogen, 44.
Bismuthines, 190, 202.
Bismuthine triethyl, 204.
Boric diethochloride, 217.
 „ ethide, 217.
 „ etho-diethylate, 218.
 „ etho-dihydrate, 218
 „ methide, 216.
Bromacetylene, 24.
Bromethylene, 103.
Bromhydrin, 104.
Brucine, 202.
Butoxyl, 5.
Butyl, 11.
Butylamine, 192.
Butylene, 17.
Butylenic bromide, 103.
 „ chloride, 103.
Butylic iodide, 83.
Butyrone, 187.

Cacodyl, 205.
Cacodylic acid, 205, 214.
 „ chloride, 205.
 „ oxide, 205.
 „ trichloride, 214.
Caffeine, 202.
Caproyl, 11.
Caprylene, 18.
Carbinol diethyl-propyl, 62.
 „ dimethyl, 60.
 „ dimethyl-ethyl, 62.
 „ dimethyl-isopropyl, 62.
 „ dimethyl-propyl, 62.
 methyl-butyl, 60.
 methyl-diethyl, 62.
Carbinol methyl-ethyl, 60.
 „ methyl-hexyl, 60.
 „ methyl-isopropyl, 60.
 „ methyl-nonyl, 60.
 „ methyl-propyl, 60.
 „ triethyl, 62.
 „ trimethyl, 62.
Carburetted hydrogen, light, 39.
Caustic antimony bases, 211.
 „ arsenic bases, 211.
 „ nitrogen bases, 211.
 „ phosphorus bases, 211.
Cerotene, 18.
Cetene, 18.
Chloracetamide, 206.
Chloral, 110.
 „ alcoholate, 110.
 „ hydrate, 110.
Chloranil, 76.
Chloraniline, 210.
Chlorether, 228.
Chlorhydrate, ethylenic, 95.
Chlorhydrin, 95, 104.
Chloride, methylic, 101.
Chlorine, action of, on the radicals of the ethylene series, 18.
Chloro-compounds of benzol, 47.
Chloroform, 100.
Chloropropionylic chloride, 142.
Chrysaniline, 199.
Cinchonine, 201.
Citramide, 209.
Citryl-triphenyl-triamide, 209.
Classification of organic compounds, 8.
Codeine, 201.
Collidine, 194.
Compound organic radicals, 9.
 „ negative radicals, hydrides of, 37, 49.
 „ oxamides, 36.
 „ positive radicals, hydrides of, 37.
Compounds, organic, definition of, 1.
Condensed diadelphic type, 5.
Conine, 193.
Constituents of organic compounds, 1.
Crotonylene, 21.
Cryptopine, 201.
Cumol, 42.
Cuprosovinylic ether, 23

Cyamelide, 32.
Cyanethine, 201.
Cyanic hydride, 49.
Cyanides, double, 29.
  ,, easily decomposable, 30.
  ,, single, 29.
Cyanmethine, 201.
Cyanogen, 26, 27.
  ,, chlorides of, 32.
Cymol, 42.

Definition of compound organic radicals, 2.
  ,, organic compounds 1
Derivatives of glycol 72.
Derivatives, substitution, of benzol, 45.
Development of formulæ, 6, 7, 8
Diacetic glycol, 189.
Diacetimide, 207.
Diacetin, 189.
Diadelphic type, 4, 5.
Dialkalamides, 209.
Diamides, 207.
  ,, constitution of, 207.
  ,, formation of primary, 208.
  ,, primary, 208.
  ,, secondary, 208.
  ,, tertiary, 208.
Diamines, 191, 195.
  ,, formation of 195.
  ,, monacid salts of, 213.
  ,, normal salts of, 213.
  ,, oxides of, 196.
  ,, primary, 195.
  ,, secondary, 195.
  ,, tertiary, 195.
Dibasic acids, 158.
  ,, anhydrides of, 184.
  ,, fumaric or acryloid series of, 166.
Dibrombenzol, 45.
Dibutylamine, 193.
Dibutyraldine, 200.
Dichloraniline, 210.
Dichlorbenzol, 47.
Dichlorhydrin, 96, 104.
Dichlorinated methylic chloride, 100.
Dichlorinated methylic ether, 87.
Diethylamine, 193.
Diethylammonic iodide, 193.
Diethylated acetone, 187.
  ,, ethylic ether, 228.
Diethylbenzol, 43.
Diethylene triammonic dichloride, 213.
  ,, triammonic monochloride, 213.
  ,, triammonic trichloride, 213
Diethyl oxamide, 209
Diethylphosphonic zincic iodide, 202
Diethyl urea, 197.
Dihydric alcohols, 70, 74.
Dimethylamine, 193
Dimethylaniline, 195
Dimethylated acetone, 187.
Dimethylcumidine, 195.
Dimethylcymidine, 195.
Dimethyloxamide, 36.
Dimethylphenylammonic chloride, 194
Dimethyltoluidine, 195.
Dimethyltolylammonic chloride, 194
Dimethylxylidine, 195.
Dinitrobenzol, 49
Diphenyl-carbonyl-oxalyl diamide, 209
Diphenyloxamide, 36
Diphenyl rosaniline 198.
Disilicic hexachloride, 219.
Disilicic oxy-hexethide, 220.
  ,, oxy-hexethylate, 220.
  ,, oxy-hexamethylate, 219.
Double cyanides, 29.
  ,, monadelphic type 5
Dyad positive radicals, 9, 16, 21, 24.
  ,, action of chlorine on, 18.
  ,, haloid ethers of, 102.
  ,, reactions of ethylene series of, 18

Elaldehyde, 100.
Epichlorhydrin, 96, 105.
Erythrite, 83.
Erythroglucin, 83.
Erythromannite, 83.
Æther, 85.
  ,, allylic, 89.

Ether amylic, 86.
„ benzylic, 89.
„ butylic, 86.
„ cuprosovinylic, 23.
„ diethylated ethylic, 228.
„ dimethacetic, 128.
„ disodacetic, 128.
„ ethylenic, 90.
„ ethylic, 85, 87.
„ ethylic amylic, 86.
„ ethylic butylic, 86.
„ glycylic, 93.
„ methylic, 85, 87.
„ methylic amylic, 85.
„ methylic ethylic, 85.
„ monosodacetic, 121.
„ phenylic, 89.
„ phenylbenzyl, 90.
„ stanntriethylic, 231.
„ sulphomethylic, 190.
„ sulphuric, 87.
„ trimethacetic, 129.
Ethers, 85.
„ formation of, 86.
„ haloid, 93.
„ haloid, of the dyad positive radicals, 94, 102.
„ haloid, of the monad positive radicals, 93, 96.
„ haloid, of the triad positive radicals, 95, 104.
„ of the dihydric alcohols, 85, 90.
„ of the methyl series, 85.
„ of the monohydric alcohols, 85.
„ of the phenyl series, 89.
„ of the trihydric alcohols, 85, 93.
„ of the vinyl series, 89.
Ethereal salts, 188.
„ salts, decomposition of, 190.
„ salts, definition of, 188.
„ salts of dihydric alcohols, 189.
„ salts of dibasic acids, 189.
„ salts of dibasic acids, acid, 189.
„ salts of dibasic acids, normal, 189.
„ salts of monobasic acids, 189.
„ salts of monohydric alcohols, 189.
Ethereal salts of tribasic acids, 189.
„ salts of tribasic acids, acid, 189.
„ salts of tribasic acids, normal, 189.
„ salts of trihydric alcohols, 189.
„ salts, production of, 188.
Ethide, boric, 217.
„ hypostannic, 230.
„ lithiomercuric, 234.
„ lithiozincic, 234.
„ magnesic, 234.
„ mercuric 225.
„ perplumbic, 231.
„ potassic, 232.
„ potassio-zincic, 234.
„ sodio-zincic, 234.
„ stannic, 225.
„ stannous, 230.
„ tellurium, 231.
„ zincic, 225.
Ethobromide, mercuric, 229.
Ethodimethide, stannic, 230.
Ethodiniodide, hypostannic, 230.
Ethohydrate, mercuric, 230.
Ethonitrate, mercuric, 234.
Ethoxyl, 5.
Ethyl, 11, 12.
Ethyl acetamide, 209.
„ acetone, 187.
„ acetyl, 187.
„ butyral, 187.
„ diacetamide, 209.
„ propionyl, 187.
„ urea, 196.
Ethylamine, 99, 192.
Ethylammonic chloride, 212.
„ iodide, 99.
Ethylamylamine, 193.
Ethylated acetone, 187.
Ethylene, 16, 20.
„ and ethylidene compounds, isomerism of, 19, 146.
„ compounds, 18.
„ diamine, 197.
Ethylene-diammonic dibromide, 196.
„ dichloride, 213.
„ monochloride, 213.
„ oxide, 196.
Ethylene diethyl diamine, 197.
„ series, 16.

Ethylene series of radicals, action of chlorine on, 18.
,, series of radicals, preparation of, 16.
Ethylenic bromide, 103.
,, chloride, 102.
,, chlorhydrate, 95, 102.
,, cyanide, 104.
,, dichloride, 95.
,, ether, 90.
,, iodide, 103.
,, iodhydrate, 102.
,, nitrile, 104.
,, oxide, 90.
,, oxide, isomers of, 91.
,, oxide, reactions of, 91
Ethylic acetate, 189.
,, borate, 217.
,, chloride, 101.
,, *α* cyanpropionate, 166.
,, *β* cyanpropionate, 165.
,, diethaceto-acetate, 186.
,, diethoxalate, 229
,, disodacetate, 185.
,, disodacetoacetate, 186.
,, ethacetoacetate, 186.
,, ether, 90.
,, ethylozincicdiethoxalate, 229.
,, iodide, 101.
,, sodacetoacetate, 186.
,, succinate, 189.
,, sulphhydrate, 59.
,, sulphide, 89.
,, trisodacetate, 186.
Ethylidene and ethylene compounds, isomerism of, 19, 146
,, compounds, 19.
,, cyanhydrate, 147.
,, dichloride, 109.
Ethylochlorether, 228.
Ethylo-zincic dinitroethylate, 229.
,, ethylic diethoxalate. 229.
Ethyl-phenyl, 43.
Ethyl-phenylamine, 193.
Ethyl-phenylammonic iodide, 193.
Ethyl-xylol, 43.

Fatty acids, normal, 115.
,, acids, secondary, 128
,, acids, tertiary, 129.
,, series of acids, 114.
Ferricyanide, potassic, 31.
Ferrocyanide potassic, 30.
Fire-damp, 39.
Formulæ, development of, 6.
,, graphic, of organic compounds, 7.
Formyl, 25.
Formyl-diphenyl diamine, 98.
Fumaric or acryloid series of acids, 166.
,, series of acids, isomerism in, 166.
Furfurine, 200.

Gaultheria procumbens, oil of, 56.
Glucose, 84.
Glycerin, 77, 78.
,, relations of, 79, 80, 81.
Glycol, acetobutyric, 73.
,, amylic, 70.
,, bromethylic, 72.
,, bromhydric, 72.
,, butylic, 70.
,, chlorhydric, 72, 102.
,, cyanhydric, 148.
,, derivatives of, 72.
,, diacetic, 71, 189.
,, diethylenic, 73.
,, diethylic, 72.
,, disodic, 72.
,, ethylic, 71.
,, hexethylenic, 73.
,, hydric ethylic, 72.
,, iodhydric, 102
,, monacetic, 72, 103, 189.
,, monosodic, 72.
,, pentethylenic, 73.
,, propylic, 70.
,, sulphur, 72.
,, tetrethylenic, 73
,, triethylenic, 73
Glycollic acetobromide, 72.
Glycols, 70.
,, polyethylenic, 73.
,, relations of succinic series to, 161.
Glycolyl, 25.
Glyoxal, 152.
Glyoxyloid series of dibasic acids, 173.
Graphic formulæ of organic compounds, 7.
Guanidine, 200.
Guanine, 200.

Haloid compounds of oxybases, 190, 210.
- ,, ethers, 93.
- ,, ethers of the dyad positive radicals, 94, 102.
- ,, ethers of the monad positive radicals, 93.
- ,, ethers of the triad positive radicals, 95, 104

Heptylene, 18.
Hexylene, 17.
Hofmann's violet, 199.
Homopyrocatechin, 74.
Hydrazobenzid, 48.
Hydride, amylic, 39, 41.
- ,, butylic, 39.
- ,, caproylic, 39.
- ,, cyanic, 49.
- ,, decatylic, 39.
- ,, dodecatylic, 39.
- ,, endecatylic, 39.
- ,, ethylic, 39, 40.
- ,, heptylic, 39.
- ,, hexylic, 39.
- ,, methylic, 39.
- ,, nonylic, 39.
- ,, octylic, 39.
- ,, oxatylic, 49.
- ,, pentadecatylic, 39.
- ,, pentylic, 39.
- ,, phenylic, 44.
- ,, propylic, 39.
- ,, tetradecatylic, 39.
- ,, tetrylic, 39.
- ,, tridecatylic, 39.
- ,, tritylic, 39.

Hydrides of compound negative radicals, 37, 49.
- ,, of compound positive radicals, 37.
- ,, of the radicals of the methyl series, 37.
- ,, of the radicals of the methyl series, preparation of, 38.
- ,, of the radicals of the phenyl series, 42.

Hydrochloric glycide, 96, 105.
Hydrocotarnine, 201.
Hydrogen, bicarburet of, 44.
Hydroquinone, 75.
Hydrosulphate of ethyl, 59.
Hypostannic ethide, 230.
Hypostannic ethodiiodide, 230.

Imides, 190, 210.
- ,, general formula of, 210.

Imidogen bases, 193.
Introduction to organic chemistry, 1.
Iodide, phosphonic, 202.
Iodhydric glycol, 102.
Iodhydrin, 93.
Iododiethide, stannic, 230.
Iodotriethide, stannic, 230.
Isobutylene, 17.
Isomeric forms of valeric acid, 126.
Isomerism in fumaric or acryloid series, 166.
- ,, in the lactic series, 143.
- ,, of ethylene and ethylidene, 146, 168.

Isopropylic alcohol, 61.
- ,, iodide, 79.
- ,, nitrile, 128.

Ketones, 184.
- ,, formation of, 185.
- ,, isomerism of, 187.
- ,, list of, 187.

Ketones of the C_nH_{2n-7} series, 188.

Lactic series of acids, relations of, to acetic series, 142.
- ,, series of acids, relations of, to acrylic series, 142.
- ,, series of acids, relations of succinic series to, 161.

Lactide, 183.
Lactoid series of dibasic acids, 172.
Lactyl, 25.
Laudanosine, 201.
Lead.
- Perplumbic chlorotriethide, 231.
  - ,, ethide, 231.
  - ,, triethohydrate, 231.

Leucin, 150.
Leukaniline, 199.
Light carburetted hydrogen, 39.
Lithiomercuric ethide, 234.
Lithiozincic ethide, 234.
Lutidine, 194.

Magenta, 198.
Magnesic ethide, 234.
Malic series of acids, 172.
Malonyl, 25.
Mannite, 84.
Marsh-gas, 39.
Marsh-gas series, hydrides of, 37.
,, type, 4.
Mauveine, 198.
Meadow-sweet, oil of, 156.
Melene, 18.
Mendius's reaction, 55.
Mercaptan, 59.
Mercury.
Mercuric amylide, 226.
,, ethide, 225, 234.
,, ethiodide, 225.
,, ethobromide, 229.
,, ethohydrate, 230.
,, ethonitrate, 234.
,, iodethide, 232
,, methide, 229, 234.
,, methiodide, 229, 234.
,, methohydrate, 230.
,, naphthide, 226.
Organo- compounds, 225, 229, 232.
Metaldehyde, 109.
Methide, aluminic, 232.
,, boric, 216.
,, mercuric, 234.
,, potassio-zincic, 234.
,, tellurium 234.
,, zincic, 228, 234.
Methoxyl, 5.
Methyl, 11.
Methyl acetone, 187.
,, benzol, 188.
,, benzoyl, 188
,, series, hydrides of the radicals of, 37.
,, series of alcohols, 52.
,, series, normal alcohols of, 52, 53.
,, series, secondary alcohols of, 52, 60.
,, series, tertiary alcohols of, 52, 62.
,, series, normal radicals of, 10.
,, series, preparation of normal radicals of, 11.
,, series, secondary radicals of, 10.
Methyl series, tertiary radicals of, 10.
,, type, 4.
,, valeral, 187.
Methylamine, 192.
Methylated acetone, 187.
Methylene chloride, 102.
,, iodide, 102.
Methylethylamine, 193.
Methylethyl-phenylamine, 194.
Methylic borate, 215.
,, chloride, 99.
,, chloride, dichlorinated, 100.
,, chloride, monochlorinated, 100
,, chloride, trichlorinated, 100.
,, iodide, 102.
,, nitrile, 119.
,, oxide (*Methylic ether*), 87.
Methylo-zincic dinitromethylate, 229
Methylphenyl, 42.
Methylphenylammonic chloride, 194
Methyl xylol, 43.
Monacetic glycol, 189.
Monacetin, 189.
Monad positive radicals, 10
,, positive radicals, haloid ethers of, 93, 96.
Monadelphic type, 4, 5.
Monalkalamides, 209.
Monamides, 206
,, formation of primary, 206
,, primary, 206.
,, reactions of primary, 207.
,, secondary, 207.
,, tertiary, 207.
Monarsines, 191.
,, formation of primary, 191.
,, formation of secondary, 193.
,, formation of tertiary, 193.
,, methyl series of primary, 191.
,, methyl series of secondary, 192.

Monamines, phenyl series of primary, 191.
  ,, phenyl series of secondary, 192.
  ,, primary, 191.
  ,, reactions of primary, 192.
  ,, recognition of primary, 195.
  ,, recognition of secondary, 195.
  ,, recognition of tertiary, 195.
  ,, secondary, 191, 192.
  ,, tertiary, 191, 193
  ,, vinyl series of primary, 191.
  ,, vinyl series of secondary, 192.
Monobasic acids, anhydrides of, 182, 183
  ,, organic acids, 113.
Monobrombenzol, 45.
Monobromorcin, 76.
Monochlorbenzol, 47.
Monochlorhydrin, 79.
Monochlorinated methylic chloride, 100.
  ,, propylic glycol, 79.
Monohydric alcohols, 52, 63, 66.
  ,, alcohols, secondary, 60.
  ,, alcohols, tertiary, 62, 67.
  ,, alcohols, normal, of the phenyl series, 66.
  .. alcohols of the phenyl series, 66.
  ,, alcohols of the vinyl series, 63.
Monomethylarsenic acid, 214, 233.
Morphine, 201.

Narceine, 201.
Narcotine, 201.
Natural alkaloids, 201.
Negative compound radicals, hydrides of, 49.
  ,, organic radicals, 9, 25.
Nicholson's yellow, 199.
Nicotine, 202.
Nitraniline, 49.
Nitrides, general formula of, 210.
  ,, negative, 210.
Nitrile, ethylenic, 104.
  ,, isopropylic, 128.
  ,, methylic, 119.
Nitriles, preparation of, 97.
Nitrobenzol, 43, 47.
Nitrocumol, 43.
Nitrocymol, 43.
Nitrogen, caustic bases of, 211.
  ,, compounds of triad, and its analogues, 190.
  ,, compounds of pentad, and its analogues, 211.
  ,, organic compounds of, 190.
Nitropentol, 43.
Nitrotoluol, 43.
Nitroxylol, 43.
Nonylene, 18.
Normal acids, 114.
  ,, acids of the acrylic series, 130.
  ,, acids of the lactic series, 135.
  ,, fatty acids, 115.
  ,, monohydric alcohols of phenyl series, 66, 67.
  ,, oleine acids of the lactic series, 139.
  ,, radicals of methyl series, 11.
  ,, radicals of methyl series, preparation of, 11.
  ,, salts of amines, 213.

Octylene, 18.
Œnanthylene, 18.
Oil of bitter almonds, 111.
  .. of Gaultheria procumbens, 56.
Oleine type, 5.
Oleic series of acids, 130.
Orcein, 77.
Orcin, 76, 77.
Organic antimonic acids, 215.
  ,, arsenic acids, 214.
  ,, arsenic chlorides, 214.
  ,, arsenic oxychlorides, 214.
  ,, bases, 191.
  ,, compounds, definition of, 1.
  ,, compounds, classification of, 8.
  ,, compounds, elements contained in, 1, 2.
  ,, compounds, graphic formulæ of, 7, 8.
  ,, compounds, notation of, 3.

Organic radicals, 3.
  „ radicals, compound, definition of, 2.
  „ radicals, negative, 9
  „ radicals, positive, 9
Organo-aluminic compounds, 232.
  „ antimony compounds 233.
  „ arsenic compounds, 233
  „ bismuth compounds, 233
  „ boron compounds, 215
  „ boron compounds, definition of, 215
  „ cadmium compounds, 232
  „ lead compounds 231
  „ magnesium compounds 232
  „ mercury compounds 229
  „ potassium compounds 227
  „ silicon compounds 215, 218
  „ sodium compounds 227
  „ tellurium compounds 231
  „ tin compounds, 230
  „ zinc compounds, 227, 232
Organometallic bodies 223
  „ bodies, constitution of 231
  , bodies, definition of, 223
  „ bodies, formation of, 225
  „ bodies, reactions of, 227
  „ bodies, types of, 232
Oxamide 36, 208
Oxamides, compound, 36
Oxatyl, 26, 32
Oxatylic hydride, 49
Oxyantimonic bases, 212
  „ bases, salts of, 214
Oxyarsenic bases, 211
  „ bases, salts of, 214
Oxybases, 190, 204
  „ arsenious, 204
  „ haloid compounds of, 190, 210.
Oxyphenol, 74.

Papaverine, 201.
Paraffin, 41.
Paraldehyde, 109
Paramylene, 18
Parvoline, 194.
Pentol, 42.
Perchlorinated methylic ether, 87
Phenyl, 15
Phenyl series, ethers of, 89
  „ series, hydrides of the radicals of, 42
  „ series monohydric alcohols of, 66
  „ series, normal monohydric alcohols of, 66
  „ series, radicals of, 14
  „ series, tertiary alcohols of, 67 68
Phenylamine, 192
Phenylene diethylic ketone 188
  „ series of radicals 24
Phenyl formamide, 98, 154
Phenylic cyanide, 98
  , hydride 44.
  „ iodide 94
Phenyl rosaniline 198
Phloroglucin 81
Phloryl 67
Phosphine diethyl 203
  „ dimethyl, 203
  „ ethyl, 203
  „ methyl, 203
  „ triethyl, 204
  „ trimethyl, 204
Phosphines, 190, 202
  „ primary 202
  „ salts of, 214
  „ secondary, 202
  „ tertiary 203
Phosphonic iodide, 202
Phosphoric triethoxide, 204
Phosphorus, organic compounds of 190
Phthalylic chloride, 188
Phycite, 83.
Picoline 194
Picroerythrin, 76.
Pinite, 84
Piperidine, 193
Polyhydric alcohols, 83
Positive compound radicals, hydrides of 37
  „ dyad radicals, haloid ethers of, 94, 102
  „ monad radicals, haloid ethers of, 93, 96
  „ organic radicals, 9.
  „ triad radicals, haloid ethers of, 95, 104.

Potassium.
Potassic cyanate, 29.
,, ethide, 232.
,, ferricyanide, 31.
,, ferrocyanide, 30.
,, succinate, 104.
,, sulphocyanate, 32.
Potassiozincic ethide, 234.
,, methide, 234.
Propione, 187.
Propoxyl, 5.
Propyl, 11.
Propylene, 17.
Propylenic bromide, 103.
,, chloride, 103.
,, iodide, 103.
,, oxide, 90.
Propylic glycol, monochlorinated, 79.
Propylic iodide, 94.
Protopine, 201.
Prussian blue, 31.
Pseudobutylene, 17.
Pseudorcin, 83.
Pyridine, 194
Pyrocatechin, 74.
Pyrogallin, 81, 82.
Pyroxylic spirit, 56.

Quercite, 84.
Quinine, 201.
Quinone, 75.

Radicals, acetylene series of, 21.
,, dyad positive, 16.
,, dyad, relations of succinic series to, 161.
,, haloid ethers of the dyad positive, 94, 102.
,, haloid ethers of the monad positive, 93, 96.
,, haloid ethers of the triad positive, 95, 104.
,, hydrides of positive compound, 37.
,, monad positive, 10.
,, monad, relations of, to fatty acids, 119.
,, negative, hydrides of, 37, 49.
,, normal, of the methyl series, 11.
Radicals, normal, of the methyl series, preparation of, 11.
,, of the phenylene series, 24.
,, of the phenyl series, 14.
,, of the phenyl series, hydrides of, 42.
,, of the vinyl series, 13.
,, organic, 3.
,, secondary, of the methyl series, 10.
,, tertiary, of the methyl series, 10.
,, triad positive, 25.
Resorcin, 74.
Rosaniline, 198.

Salts, ethereal, 188
Secondary monohydric alcohols, 60.
,, radicals of the methyl series, 13.
Silicic aceto-triethylate, 220.
,, acetylate, 220.
,, chloroform, 218.
,, chlortriethide, 220.
,, chlortriethylate, 220.
,, dichlorethide, 220.
,, dichlorethylate 220.
,, dieth-ethylate, 220.
,, dietho-chlorethylate, 220.
,, diethoxide, 220.
,, dimethylate ethylate, 220.
,, ethide, 221.
,, ethotriethylate, 220.
,, ethylate, 220.
,, hydrotriethylate, 220.
,, methide, 219, 221.
,, methylate, 220.
,, trichlorethide, 220.
,, trieth-ethylate, 220.
,, triethohydrate, 222.
,, triethylate amylate, 220.
Silicoformic anhydride, 218.
Siliconylic acetate, 220.
,, alcohol, 220.
,, chloride, 220.
Silicopropionic acid, 222.
Single cyanides, 29.
Sodio-zincic ethide, 226, 234.
Spirit of wine, 57.
Stearin, 78.
Stibine, triamyl, 204.
,, triethyl, 204.
,, trimethyl, 204.

Stibines, 190, 202.
  „ salts of, 214.
Strychnine, 202.
Styrol, 157.
Substitution derivatives of benzol, 45.
Succinamide, 208.
Succinic series of acids, 159.
  „ series, relations of, to acetic series, 162.
  „ series, relations of, to dyad radicals, 161.
  „ series, relations of, to lactic series and to glycols, 161.
Succinimide, 207, 210.
Succinylic chloride, 187.
Sulphophenyl urea, 197.
Sulphur alcohol 59.
Sulphuric diethoxide, 89
Sulphurous diethoxide, 89.
  triethylo-iodide, 89
  „ triethylo-hydrate, 89.

Tartaric or glyoxyloid series of acids, 173.
Tellurium ethide, 231.
Tellurous diethoxide, 231, 233.
  „ diethiodide, 231, 233
  le, 231.
Tertiary acids of the fatty series, 114, 129
  „ diamines, 195.
  „ monohydric alcohols, 62, 67.
  „ monamides, 207.
  „ monamines, 191, 193.
  „ monarsines, 211.
  „ radicals of the methyl series, 10.
Tetrachlorinated methylic ether, 87
Tetramines, 191.
Tetrethylammonic hydrate, 211.
Thebaine, 201.
Theine, 202.
Theobromine, 202.
Thialdine, 200.
Tin.
  Distannic hexethoxide, 233.
  Hypostannic ethide, 230.
    „ ethodiniodide, 230.
  Stannic chlorotriethide, 230.
    „ dichlorethide, 226.

Tin.
  Stannic ethide, 225.
    „ ethodimethide, 230.
    „ ethophenyl dichloride, 235.
    „ iododiethide, 230.
    „ iododimethide, 235.
    „ iodotriethide, 230.
    „ iodotrimethide, 235.
    „ methide, 235.
    „ phenyl-triethide, 235.
    „ triethohydrate, 233.
  Stannous ethide, 230.
  Stanntriethylic alcohol, 231.
    „ chloride, 231.
    „ ether 231
    „ haloid ether, 231.
Toluidine, 192.
  „ blue, 198.
Toluol, 42.
Tolyl, 14.
Tolylamine, 192.
Triacetin, 189.
Triad positive radicals, 25.
  „ positive radicals, haloid ethers of, 104
Triadelphic type, 4, 5.
Trialkalamides, 209.
Triamides, 208.
  „ primary, constitution of, 208
  „ secondary and tertiary, 209.
Triamines, 198
  „ diacid salts of, 213.
  „ monacid salts of, 213.
  „ normal salts of, 213.
Triamylamine, 194.
Tribasic acids 177.
  „ acids, aconitic or acryloid series of, 177.
  „ acids, citric or lactoid series of, 178
  „ acids, tricarballylic or acetoid series of, 177.
Tribrombenzol, 46.
Tribrombenzol hydrobromate, 46.
Tribromopyrogallin, 83.
Tribromorcin, 76.
Tributylamine, 194.
Trichloraldehyde, 110.
Trichloraniline, 210.

Trichlorbenzol, 47.
Trichlorhydrin, 96, 105.
Trichlorinated &c. amines, 190, 209.
   „ methylic chloride, 100.
Trichlororcin, 76.
Triethylamine, 194.
Triethylammonic iodide, 193.
Triethyl arsine, 204.
   „ phosphine, 203.
   „ phosphonic iodide, 203.
   „ rosaniline, 199.
   „ silicol, 220.
   „ stibine, 204.
Trihydric alcohols, 51, 77.
   „ ethers of, 93.
Triiodorcin, 76.
Trimethylamine, 194.
Triphenyl rosaniline, 198.
Tritolyl rosaniline, 198.
Turnbull's blue, 32.
Type, ammonia, 4, 5.
   „ ammonic chloride, 4, 5.
   „ condensed diadelphic, 5.
   „ diadelphic, 4.
   „ double monadelphic, 5.
   „ marsh-gas, 4.
   „ methyl, 4.
   „ monadelphic, 4, 5.
   „ olefine, 5.
Type, triadelphic, 4, 5.
Types of organic compounds, 4.

Urea, 196.
   „ derivatives of, 197.
   „ formation of, 196.
   „ reaction of, 197.
Urea a diamine, 197.

Valerylene, 21.
Vinylic bromide, 103.
Vinyl series, ethers of the, 89.
   „ series, monohydric alcohols of the, 63.
   „ series, radicals of the, 13.

Xylol, 42.

Zincic amide, 229.
   „ amylide, 234.
   „ dinitro-ethylate, 228.
   „ ethide, 225, 234.
   „ ethiodide, 227.
   „ ethoethylate, 227.
   „ ethylate, 224.
   „ methide, 234.
   „ methide ethylate, 229.
   „ methyldithionate, 228.
   „ propionate, 228.
   „ succinate, 224.

END OF VOL. II.

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